MIGRATION OF POLYURETHANE ADHESIVES USED IN FLEXIBLE FOOD PACKAGING

Sally Bartram

A thesis submitted to De Montfort University for the degree of Doctor of Philosophy in the School of Applied Sciences

Department of Chemistry
De Montfort University
The Gateway
LEICESTER
LE1 9BH

February 2000

DECLARATION

The research work was carried out between December 1996 and January 2000 and unless otherwise accredited, the work was carried out by the author. No portion of the work referred to in this thesis has been submitted in support of an application for another degree or qualification of this or any other university or institute of learning.

signed/ candidate/ date 10/4/00

signed/ G Lawson (1st supervisor)/ date 11/4/00

signed/ E D Woodland (2nd supervisor)/ date 11/4/00

To my best friend Sarah.

ABSTRACT

Polyurethane (PU) adhesives are used to produce laminates for many flexible food packaging applications and consumer safety demands the monitoring of any possible migrants into foodstuffs. PU adhesives are reactive systems formed by the reaction of a polyol (polyether or polyester) and an aromatic diisocyanate in the presence of additives, eg catalysts, pH adjusters etc. to enhance the properties or speed of cure of the adhesive. In the work place PU adhesives are dispensed either solvent based, in ethyl acetate or solvent free in a liquid derivative of the diisocyanate. Although the PU adhesives are not used in direct contact with foodstuffs the potential for migration through the inner layer of the laminate is still prevalent, thus the analysis of migrants is required especially in view of the toxicological effects of the diisocyanate component. A number of commercially available flexible laminates were analysed together with the corresponding PU adhesive systems. Representative samples of both solvent free and solvent-based adhesive systems were studied. Migration tests were performed using EU specified food simulants and the exposure conditions cited in EU legislation. Migration of the aromatic diisocyanate and /or diamine (the hydrolysis product) was monitored using a colorimetric diazotisation (Marcali) method with solid phase extraction. Results showed that migration levels from solvent-based systems were lower than the EU residue limits (for NCO moiety) whilst data for solvent free adhesives were greater than this value. Diamine levels were also determined over time after lamination, these studies provided decay curves showing decreasing amine levels with increasing time post lamination. MALDI-TOF-MS was also used to investigate the migrants and traces identical to those from the starting polyol components were obtained. MALDI was used to identify polyol species in the migrants but was unable to provide any quantitative data. An HPLC method, using derivatisation of the polyol with phenyl isocyanate was developed to quantify the polyether oligomers. Migration levels of polyether oligomers were determined for a number of commercial laminates and were found to be of the order 50-100 $\mu g/dm^2$. Migration of polyether species through polyethylene film was confirmed and was dependent on the structure of the oligomers. Analysis of the additive migrants using GC-MS found the presence of branching agents, chain extenders and siloxanes used for chemical resistance.

ACKNOWLEDGEMENTS

I would like to thank MAFF for funding this work and making it all possible. My supervisor Dr Graham Lawson for his guidence and faith in me. Also the technicians at De Mortfort university for their help and advice, especially Trevor Brown, Jayshree Bhuptani and Norma Garrington.

A big thank you must go to Terry Cadby for providing samples and giving up hours to discuss current trends within industry and offer first rate technical support.

On a personal level I would like to thank my parents and Adam for their encouragement and my friends for listening to all my moans.

Finally on both a work and personal level Dr Ann Bonell. For helping me through some difficult times and without whom I have no doubt this thesis would never have been written.

CONTENTS

List of Figures

List of Reactions

List of Structures

List of Tables

Abbreviations

AA	Adipic acid
ALU	Aluminium
BHT	Butylatedhydroxytoluene
BLLDPE	Block Low Linear Density Polyethylene
CAP	Caprolactone
CEN	German Institute of Standardisation
CONC	Concentration
CSL	Central Science Laboratory
DBA	Dibutylamine
DEG	Diethyl glycol
DMU	De Montfort University
DNB	3,5-Dinitrobenzoyl
EC	European Community
EEC	European Economic Community
EG	Ethylene glycol
ELSD	Evaporative Light Scattering Detection
EU	European Union
FPA	Flexible Packaging Association
GC	Gas Chromatography
HDA	Hexamethylene diamine
HDPE	High Density Polyethylene
HDI	Hexamethylene diisocyanate
HECE	2-Hydroxyethyl carbamic acid-2-aminoethylester
HMDI	Hydrogenated diphenyl methane diisocyanate
HPLC	High Performance Liquid Chromatography
IBA	Isobutyraldehyde
IPDI	Isophorone diisocyanate
LDPE	Low Density Polyethylene

LLDPE	Low Linear Density Polyethylene
MAFF	Ministry Of Agriculture Fisheries And Food
MALDI	Matrix Assisted Laser Disorption/Ionisation
MAMA	9(-Methlaminomethy) anthracene
MDA	Methylene dianiline
MDI	Diphenyl methane diisocyanate
MEA	Ethanolamine
MET	Metallised
MS	Mass Spectrometry
MWT	Molecular Weight
NEDD	N-(-1-Napthyl) ethylene diamine dihydrochloride
NPG	Neopentyl glycol
PE	Polyethylene
PEG	Polyethylene glycol
PET	Polyethylene Terephthalate
PMDI	Polymeric diphenyl methane diisocyanate
PP	Polypropylene
PPG	Polypropylene glycol
PU	Polyurethane
PVDC	Polyvinylidene chloride
RI	Refractive Index
RMM	Relative Molecular Mass
SEC	Size Exclusion Chromatography
SPE	Solid Phase Extraction
SSIMS	Static Secondary Ion Mass Spectrometry
TDA	Toluene diamine
TDI	Toluene diisocyanate
TOF	Time of Flight
TLV	Threshold Limit Values
TRI	Trimethylolpropane

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

Plastics have become a familiar sight in food packaging, due to their low cost, light weight and good durability. Also in recent years many changes both demographically and socially have influenced the rapid growth of plastics in food packaging materials. The opening of out-of-town supermarkets and the increase in monthly paid salaries has led to larger one off shopping trips where food is purchased weeks in advance of consumption rather than day to day shopping at smaller specialised shops for consumption within days e.g. butchers, grocers and bakery. Social changes have led to an increase in 'convenience meals', prepared meals stored and cooked in the packaging material.

These factors have placed greater demands on the properties of the food packaging to increase shelf life of the foodstuff and to be stable over a range of cooking and storage temperatures. A diverse range of polymers are used for food packaging including polyolefins, polyesters and polyamides. However in some cases, one plastic alone is unable to meet the specific requirements of the foodstuff and combinations of films are employed. In these cases a polyurethane adhesive is used to bond the substrates and provide a flexible laminate.

Since the packaging materials come into direct contact with the foodstuff it is possible for their mobile components to migrate into the packaged products. To avoid any health risk to the consumer, the use of plastic packages and articles intended to come into direct contact with foodstuffs is governed by very strict legal regulations. According to article 2 of the European Economic Community (EEC) Directive 89/109/EEC (formerly 76/893/EEC), plastic materials and articles intended to come into contact with foodstuffs should not, under normal or foreseeable conditions of use, transfer their constituent parts to foodstuffs in quantities which could endanger human health or bring about unacceptable changes in the foodstuff.

Currently all of the directives promulgated by the European Commission (EC) are concerned with the content and possible migration of plastics with no direct reference to the adhesives used in food packaging materials. In the case of polyurethane adhesives potential migrants include low molecular weight monomers, oligomers and additives.

1.1.1 Aims

To determine the identity of and the extent to which polyurethane adhesive components migrate into food.

1.1.2 Objectives

The main objectives of this work have been:

1, To establish chromatographic and spectroscopic methods in order to characterise and quantify potential migrants from polyurethane adhesives used in commercial laminates for flexible food packaging.

2, To determine the change in selected migrants from these reactive systems as a function of time after lamination.

3, To develop and apply chromatographic methods for the separation and identification of compounds migrating from model polyurethane systems.

4, To establish chromatographic methods for the characterisation and quantification of migrants from commercial laminate samples.

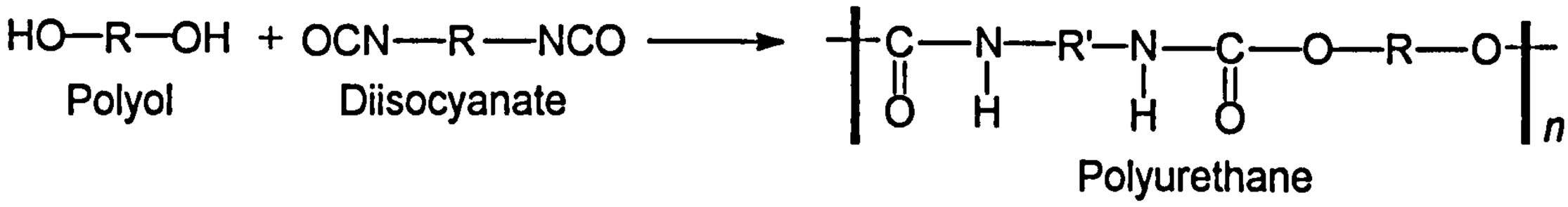
1.2 POLYURETHANES

Polyurethanes were first discovered in 1937 by the German chemist Otto Bayer[1] who refluxed aliphatic diisocyanates and aliphatic diols to build high molecular weight linear polymers. Since that date polyurethanes have grown to become among the most versatile of polymers with production by weight increasing by 450% from 1975 to 1989[2]. The main reason for this growth is the astonishing range of polymeric products; such as elastomers, fibres, rigid, flexible and semi-rigid foams, solid plastics, coatings and adhesives[3]. This multitude of products is reiterated in the diversity of applications; different forms of elastomer are used in the production of items such as sealants, shoe soles, sports equipment and car bumpers. Polyurethane fibres are commonly referred to as spandex fibres or the better known generic name Lycra, which is used in hosiery products, swim wear and sports wear. Rigid foams act as excellent thermal insulation materials used in a range of applications ranging from buildings to the modest domestic refrigerator. Flexible foam is used to manufacture comfortable and durable mattresses and seating[4]. Adhesives are utilised in textiles, lamination, construction[5], furniture and footwear[2]. Polyurethanes are also widely used in medicine as biostable implants and more recently as smart surgical dressings that promote healing, reduce scarring and allow wounds to breathe without drying out. Polyurethane foams account for some 90% of the total polyurethane market. Of the remainder 6% are coatings, adhesives and sealants.

Unlike the manufacture of the majority of thermoplastics the polymerisation of most polyurethanes is carried out by the converter and not by the chemical manufacturer. The converter bonds the films to form a laminate for use by the food industry.

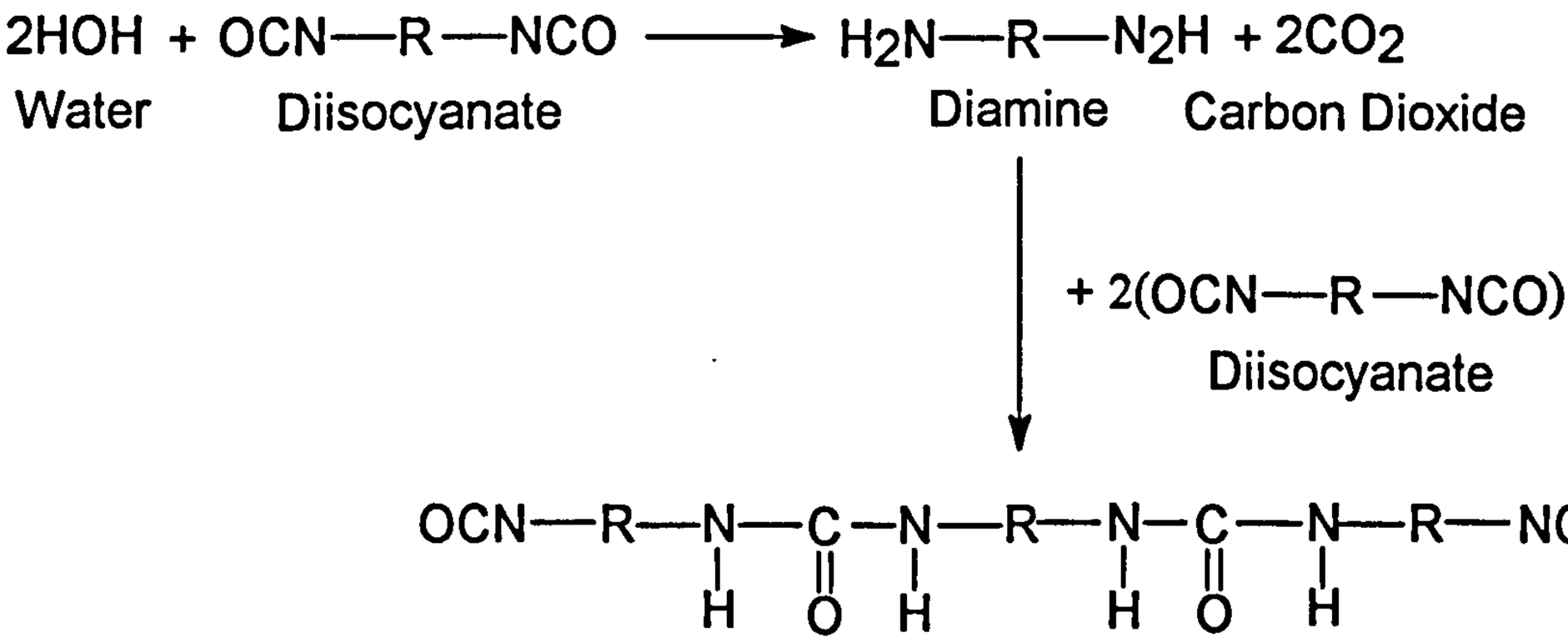
Polyurethanes are based on the exothermic reaction of polyisocyanates with polyol molecules, containing hydroxyl groups. This addition reaction produces a carbamate group, a synonym of urethane. Due to the high reactivity of the isocyanate group and its affinity to react with active hydrogen groups, other functional groups such as esters, ethers, amides, biurets and allophanates frequently appear in the polymer, hence polyurethane is a generic term for a polymer containing urethane (-NHCOO-) groups.

Reaction 1.1: Basic urethane formation



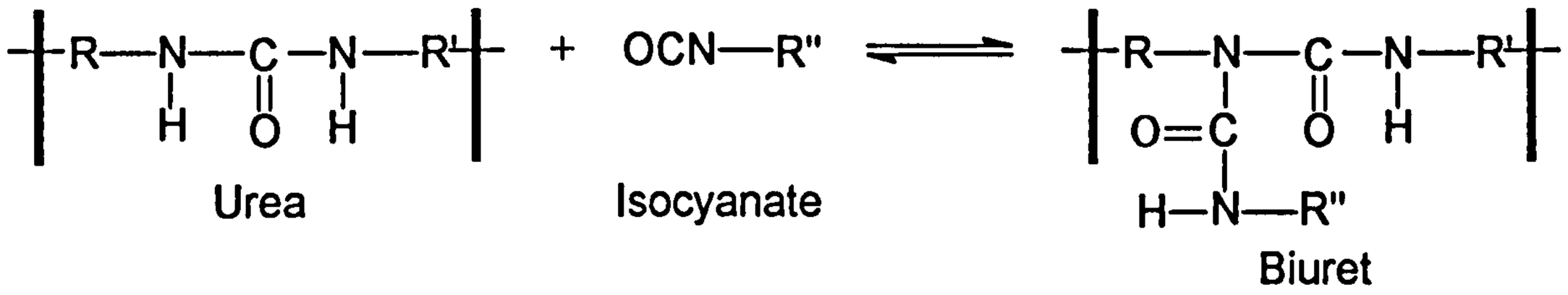
A general rule of this step growth polymerisation is that if the diisocyanate is reacted with a diol, a linear polymer will result, and if a polyol containing more than two hydroxyl groups is used a branched or cross linked polymer is formed. However cross linking can also result from further reactions of urethane groups with isocyanate groups to form urea, allophanate or biuret. Cross linking in a polymer leads to a rigid polymer with a random arrangement of molecules. Cross links are the covalent bonds between molecules and their presence and density have profound influence on both the chemical and mechanical properties of the final product. The degree of cross linking affects the polymers resistance to high temperatures and solvation although they tend to be brittle.

Reaction 1.2: The formation of diisocyanatopolyurea

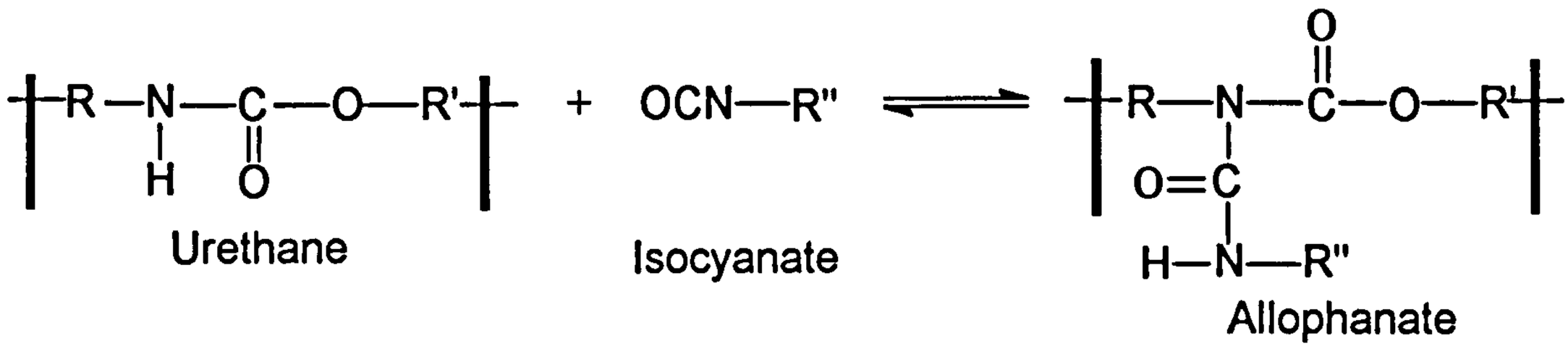


A diisocyanatopolyurea

Reaction 1.3: The formation of biuret



Reaction 1.4: The formation of allophanate



Relatively few basic isocyanates and a range of polyols of different molecular weights and functionalities are used to produce the whole spectrum of polyurethane materials. Additionally several other chemical reactions of isocyanates are used to modify or extend the range of isocyanate based materials.

1.3 DIISOCYANATES

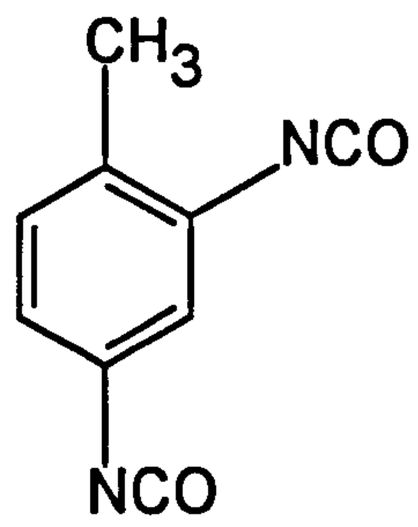
In polyurethane formation di-functional diisocyanates are used, although these are more generally referred to as isocyanates. The isocyanate component can be split into two classes; aromatic and aliphatic, of these several are available but about 95% of all polyurethanes are based on two aromatic forms; toluene diisocyanate (TDI) and diphenyl methane diisocyanate (MDI) and its derivatives. Generally aromatic isocyanates are much more reactive than the aliphatic series[4]. The manufacture of isocyanates involves treating amines with phosgene. However due to the toxicity of phosgene, an alternative method has been sought since the early 1970's, although to date attempts to produce TDI and MDI by alternative cost effective means have failed.

All the common industrial isocyanates have low threshold limit values (TLV's) and can cause sensitisation by inhalation, over exposure can cause chemical bronchitis (isocyanate asthma) in sensitised individuals[6]. However improvements in safe handling, the introduction of regular lung function tests for those working with the chemicals, and the replacement of the highly volatile TDI for isocyanates with much higher boiling points has reduced the risk of sensitisation.

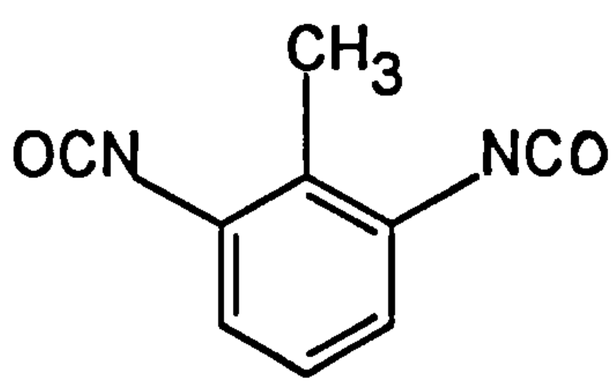
1.3.1 Aromatic diisocyanates

TDI products include flexible foams, cast elastomers and coatings. It is generally used in an 80:20 blend of 2,4 and 2,6 isomers respectively. The isocyanate in position four is eight to ten times more reactive than that in position two at room temperature, thus 2,4-TDI is the most reactive. Due to the high vapour pressure and hazardous toxicological effects of TDI it is replaced wherever possible with MDI and its derivatives. However it is unlikely that it will be phased out completely due to its superior reaction properties.

Structure 1.1: The isomers of Toluene diisocyanate



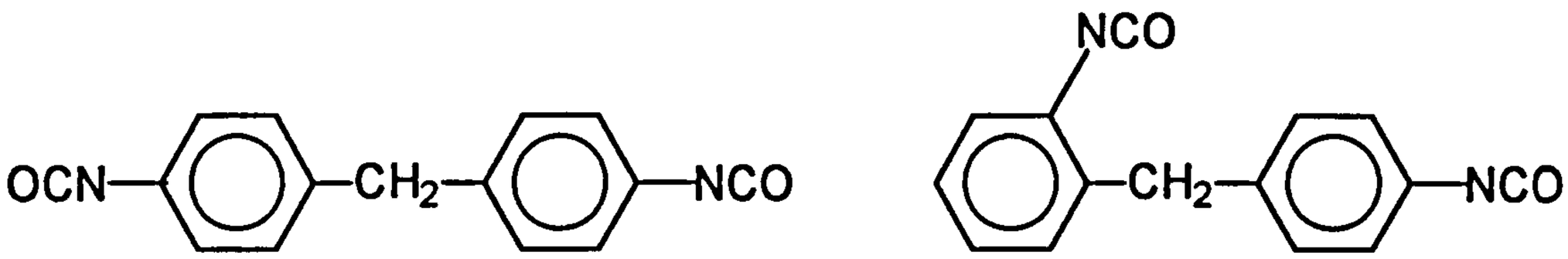
2,4 TDI



2,6 TDI

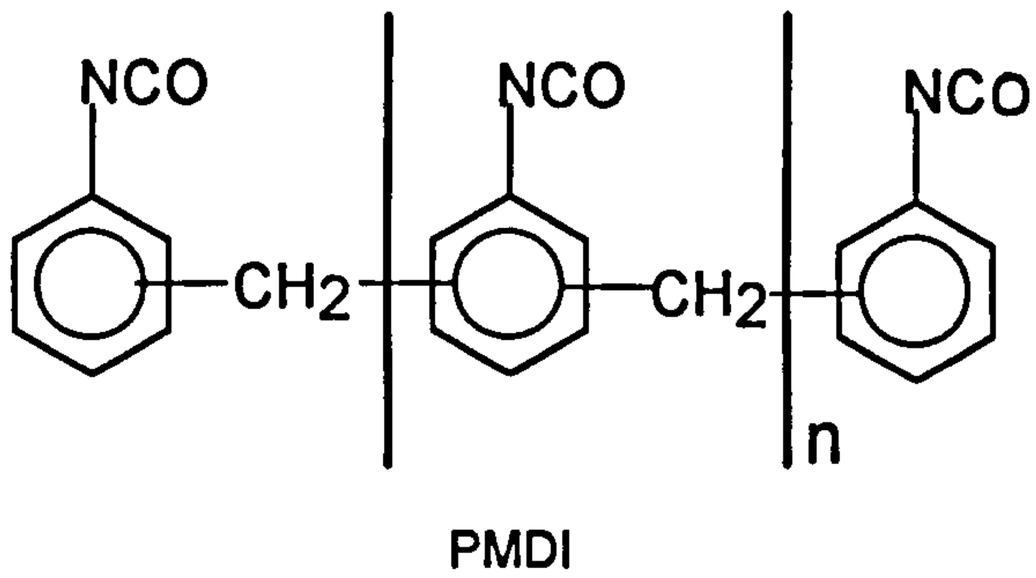
The major application of MDI is in the manufacture of polyurethane elastomers. A derivative of MDI, polymeric MDI (PMDI) is used in the manufacture of rigid foams and adhesives. Commercial MDI contains about 98% of the more reactive 4,4' isomer, the remainder being mainly the 2,4' isomer with trace amounts of the 2,2' isomer[7].

Structure 1.2: The isomers of Diphenyl methane diisocyanate



In the production of MDI, aniline and formaldehyde are reacted in the presence of hydrochloric acid to form a mixture of oligomeric amines, which are phosgenated to yield PMDI and pure MDI. The latter can be removed by continuous thin film or climbing film vacuum distillation. The viscous liquid distillation residue is referred to as PMDI although it contains only 50% of polymeric MDI and 50% of oligomeric isocyanates with functionality of three or higher and a lower vapour pressure than pure MDI.

Structure 1.3: Polymeric MDI



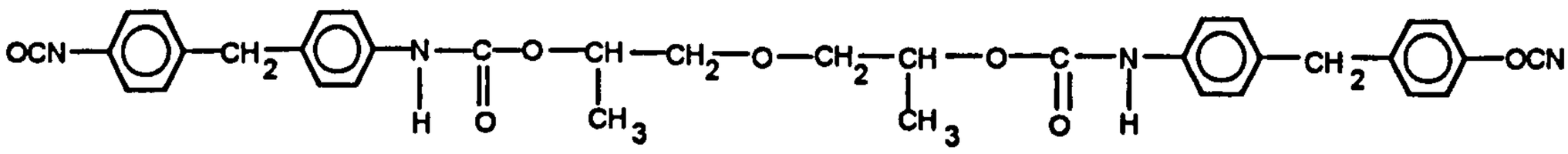
At room temperature pure MDI is a solid which is unfavourable in the production of polyurethanes. Thus as well as using PMDI, liquid MDI can be derived in a number of ways.

A lot of polyurethane applications employ the use of such a liquid derivative in the form of isocyanate terminated adducts or prepolymers, with an available isocyanate content in the range from about 3% to about 6% by weight, although isocyanate

contents of over 10% are sometimes used. The MDI prepolymer is made by pre-reacting MDI with a long chain polyol usually at a ratio of 2 :1, NCO:OH. These adducts and prepolymers can be produced with relatively low content of free, unreacted diisocyanate. The final polyurethane is then produced by reacting the prepolymer with a short chain polyol together with any minor additives. The formation of the final polyurethane will contain hard and soft segments. The hard segments are formed by reacting the isocyanate with the short chain polyol and are rigid and polar, while the soft segments consist of long polyol chains and are flexible and non-polar. This difference in polarity contributes to phase separation which produces hard and soft segment domains in the final structure. The hard domain is responsible for the rigidity of the polyurethane whereas the soft domain is responsible for the flexible and elastic properties of the polyurethane. Polyurethane adhesives have relatively few hard segments and their properties are mainly determined by the soft segments. The ratio of hard / soft segments determines the thermal, mechanical, surface and adhesion properties of the polyurethane. An increase in the amount of hard segments reduces the extent of phase separation, crystallinity, and the degree of secondary interactions between polyurethane chains within the polyurethane.

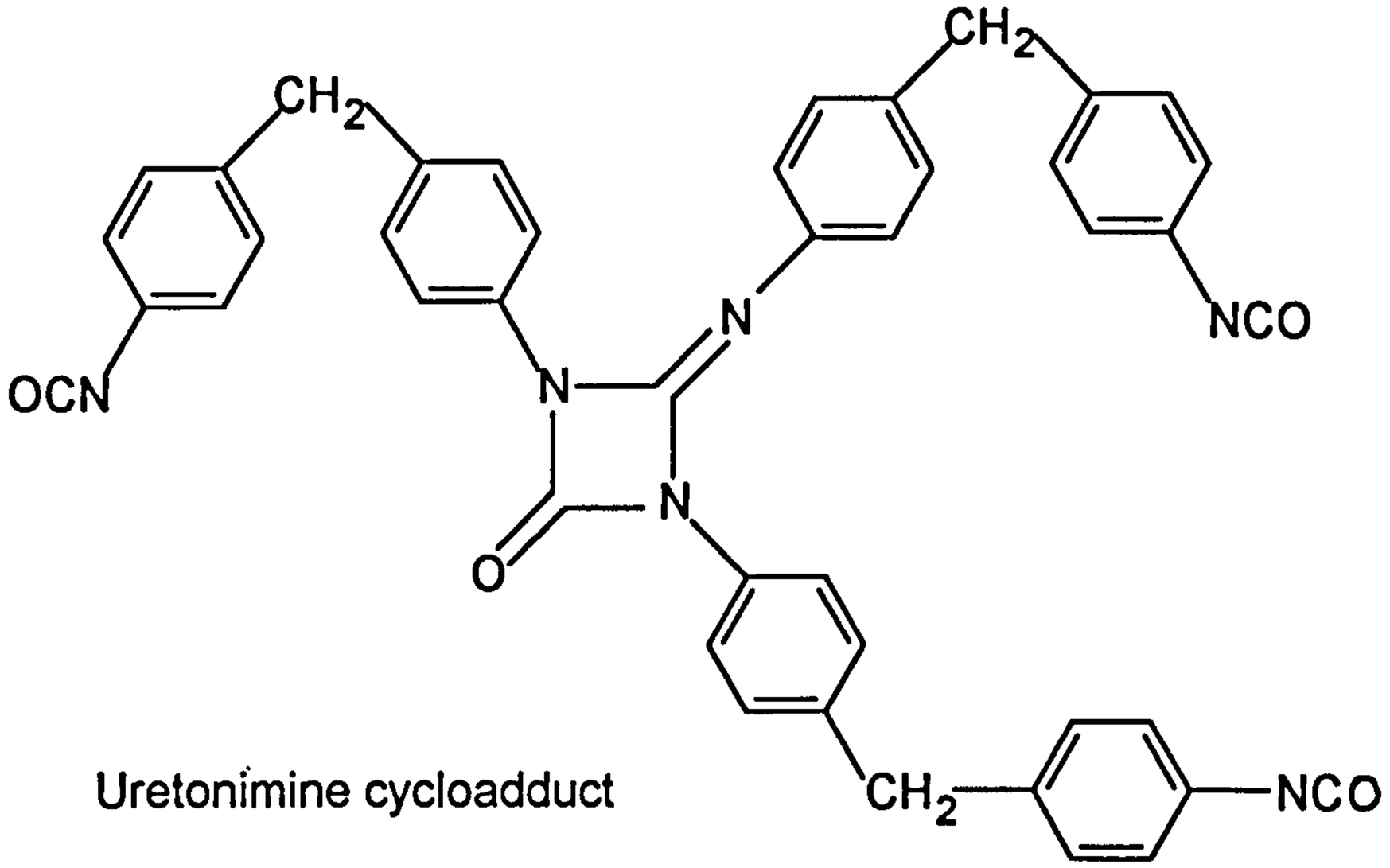
The formation of modified pure MDI is also used to overcome the problem of the isocyanate being solid at room temperature. The isocyanate is reacted with a small amount of glycol to yield a solution of diurethanes having isocyanate end groups[6]. Unlike the formation of the prepolymer these diurethanes are reacted with short chain glycols and so contain hard segments which often result in more rigid polyurethanes.

Structure 1.4: Modified pure MDI



Another liquid MDI derivative is produced by converting some of the isocyanate groups into carbodiimide groups which react with the excess isocyanate to form small amounts of uretonimine-linked tri-functional 4 membered ring cycloadducts which is lower the overall melting point of the isocyanate.

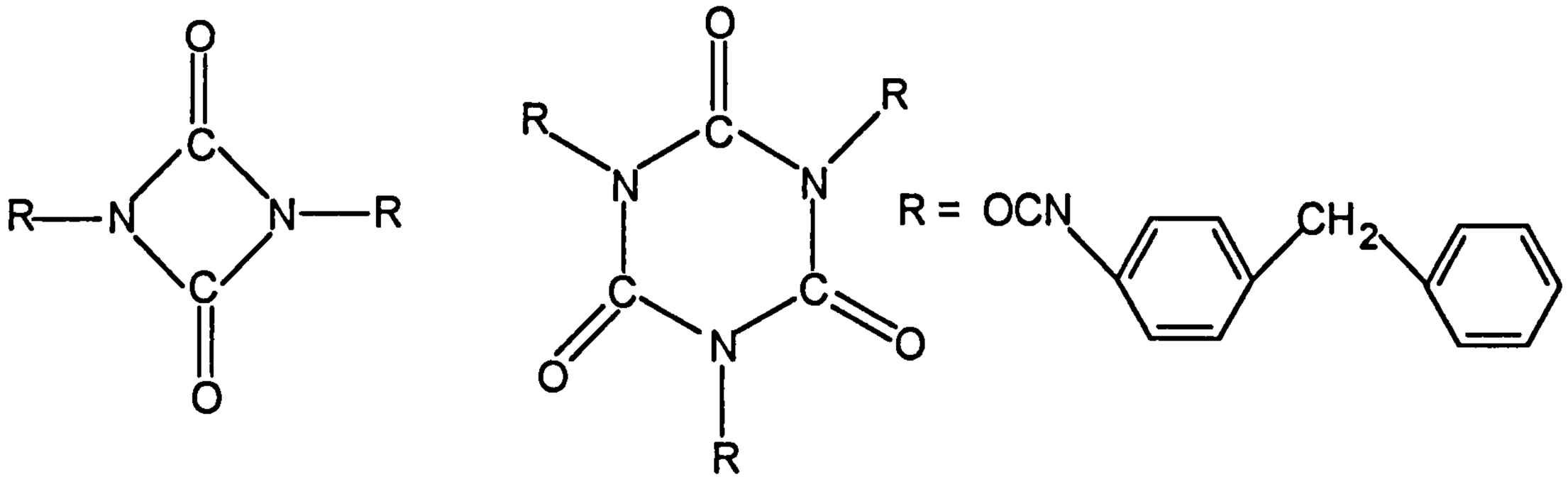
Structure 1.5: Uretonimine cycloadduct



Uretonimine cycloadduct

Pure MDI has a tendency to form uretidinediones (dimers) and isocyanurates (trimers) when stored, especially in the presence of base catalysts. The rate of self-polymerisation depends on the electronic or static influences of ring substitution. MDI dimerises slowly on standing at room temperature. Dimerisation is an equilibrium reaction and dissociation occurs at elevated temperatures, whereas trimerisation is not an equilibrium reaction and can be important in the urethane industry as it leads to branching and cross linking of the polymer. Isocyanurates can also be formed by heating both aromatic and aliphatic isocyanates to give very stable branching, as the reaction is not easily reversed.

Structure 1.6: The dimer and trimer of MDI



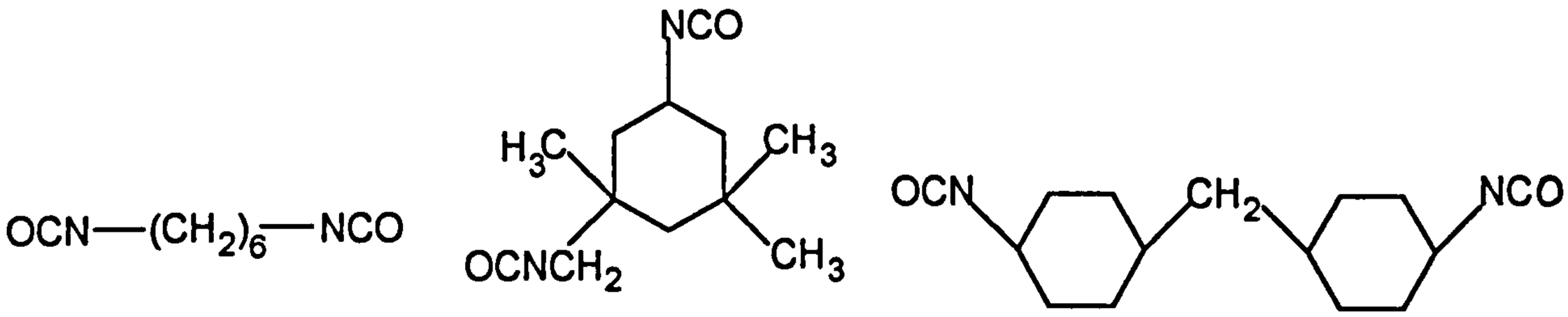
Uretidinedione (dimer) Isocyanurate (trimer)

Polyurethanes based on aromatic isocyanates tend to yellow gradually on exposure to daylight[8]. EG Beachell and Ngoc Son[9,10] showed that colour formation could be due to the oxidation of pre-existing amino groups, followed by further oxidation of amines, and the formation of coloured products, such as polypseudourea ether. It has been found that this process can be slowed by the use of additives or the replacement of the labile hydrogen in the urethane group with methyl or benzyl groups. This degradation and yellowing can also be avoided by the use of aliphatic isocyanates as it only occurs in the aromatic isocyanate series.

1.3.2 Aliphatic diisocyanates

These colour stable isocyanates are often used for coatings and elastomer applications. They account for less than 5% of the total isocyanate market and this is because aliphatic isocyanates are more expensive than aromatic isocyanates. The major aliphatic isocyanates are hexamethylene diisocyanate (HDI) Isophorone diisocyanate (IPDI) and hydrogenated MDI (HMDI).

Structure 1.7: Common aliphatic diisocyanates



HDI IPDI HMDI

The starting chemical for HDI is the inexpensive hexamethylene diamine (HDA), the monomer for nylon 6,6. The diamine is completely dried before phosgenation which is conducted in chlorobenzene. Because of its high vapour pressure HDI is converted into derivatives such as biurets or triisocyanates prior to use. IPDI is based on isophorone chemistry, It has a primary and secondary isocyanate group which facilitate derivative formation, the isophorone is produced by the trimerisation of acetone. The major isomer of IPDI is the *trans* configuration. IPDI is traditionally used for retort packaging for high temperature applications. The starting diamine for HMDI is MDA, which is obtained from aniline and formaldehyde using a large excess of the former. Hydrogenation of MDA affords a mixture of three stereoisomeric diamines: the ratio of these isomers depends mainly on the reaction temperature[7].

1.4 POLYOLS

A wide range of polyols are used in polyurethane manufacture, but in general these fall into two classes; hydroxyl terminated polyethers and polyesters. The former are the most popular accounting for about 90% of the polyurethane market, probably due to the high expense of the latter [4]. The choice of polyol, especially the size and flexibility of its molecular structure and its functionality, controls to a large extent the degree of cross linking achieved in the polymer formed. That degree of cross linking has a dominant effect on the stiffness of the polymer: to obtain a rigid foam there must be a stiff polymer network and, hence, a high degree of cross linking: for flexible foam a

proportionally lesser degree of cross linking is needed. In its adhesive form for flexible food packaging, the polyurethane must be flexible.

1.4.1 Polyether polyols

Polyether polyols with terminal hydroxyl groups are produced by the addition of cyclic ethers especially ethylene oxide and propylene oxide to polyfunctional 'starter' molecules (Table 1.1) in the presence of a catalyst, resulting in poly (ethylene glycol) (PEG) and poly (propylene glycol) (PPG) respectively. Poly (ethylene glycol) contains primary hydroxyl groups in the ethylene oxide repeat units and consequently this polymer will be more reactive than the secondary hydroxyl group in the propylene oxide unit of poly (propylene glycol). The molecular weight of the PEG appears to be controlled by the catalyst used and the polymerisation conditions [11]. Such catalysts include various alkyls and alkoxides of aluminium, zinc, magnesium and calcium, and hydrates of ferric chloride, bromide and acetate. The most common reaction is the anionic (basic) polymerisation of propylene oxide with a starter molecule, using potassium hydroxide as the catalyst (Reaction 1.5).

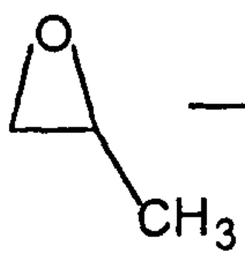
Polyethers from ethylene oxide alone are very regular in structure and yield polyurethanes with too great a tendency to harden, but those from polypropylene oxide form the basis of rubbery foams with excellent properties. Hence, ethylene oxide based polyethers tend to be used for rigid foams while propylene oxide based polyethers are used in flexible foam and adhesive applications.

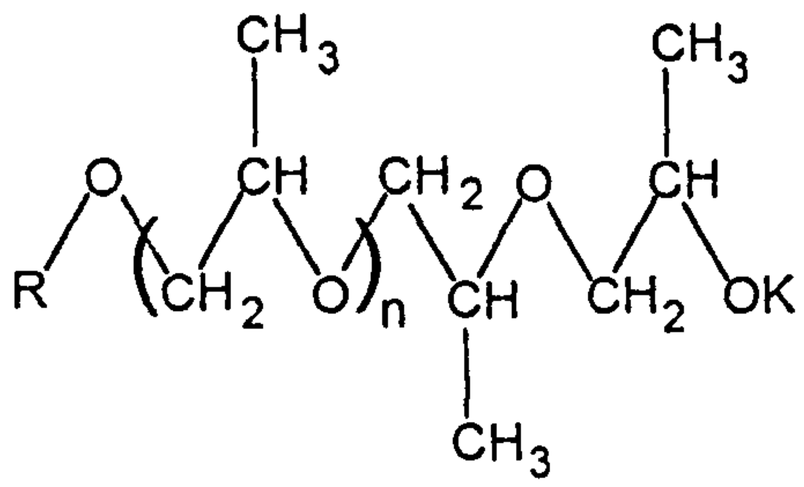
Reaction 1.5: Polymerisation of propylene oxide in basic conditions.

1 $ROH + KOH \longrightarrow ROK + H_2O$

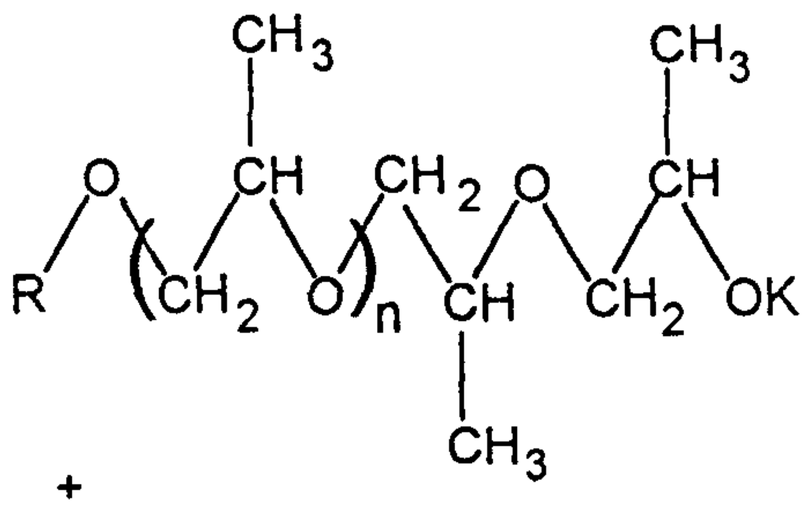
'Starter' Alkoxide ion

Propagation:

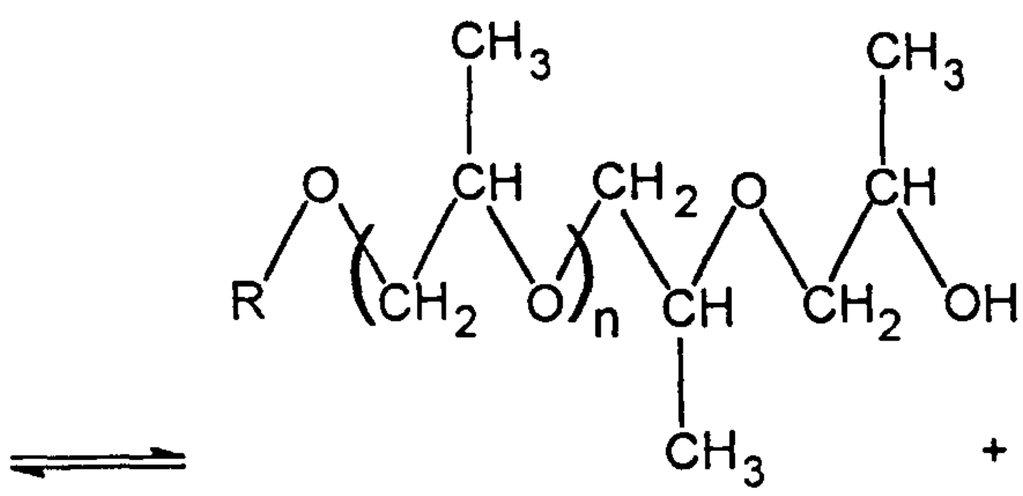
2 $ROK + n+1$ 



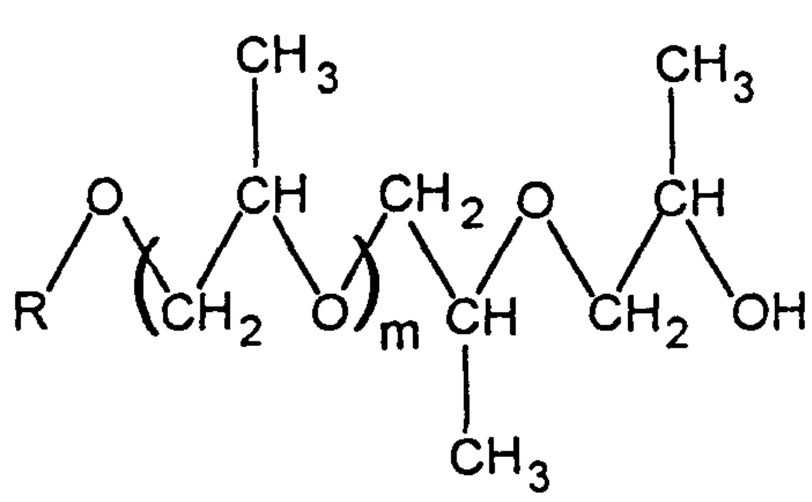
3

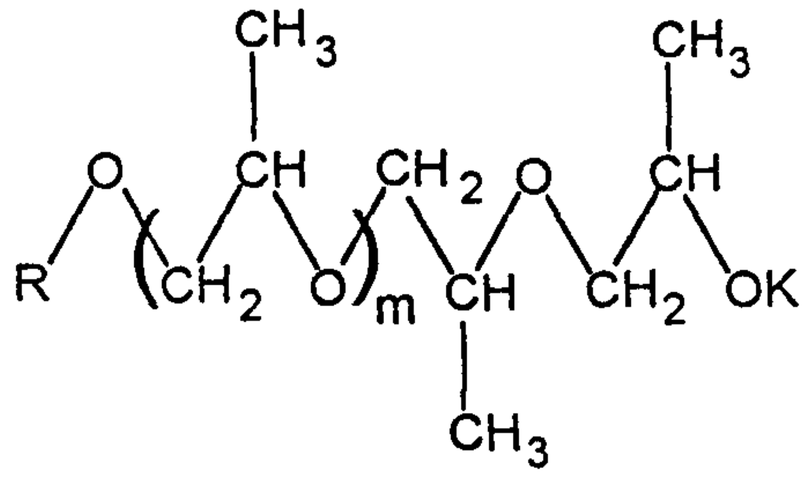


+



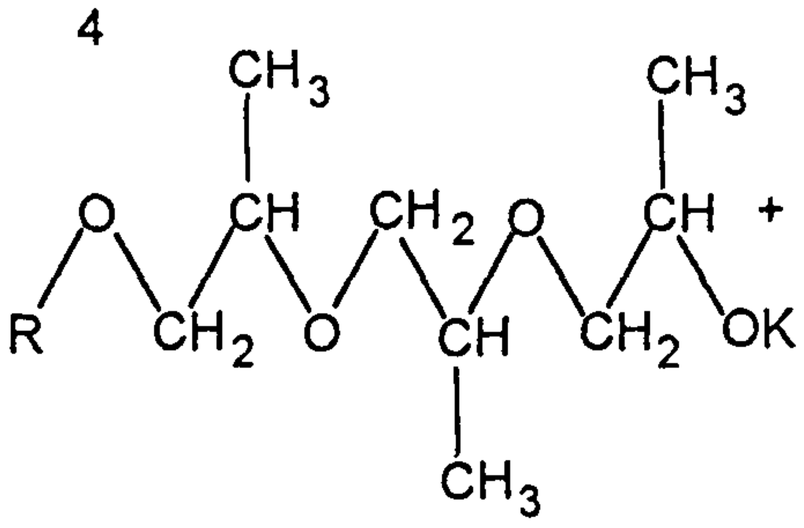
+



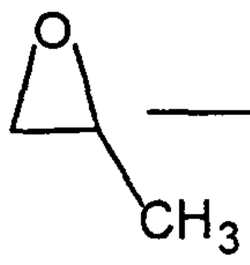


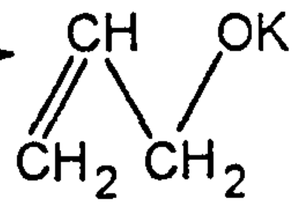
+

4



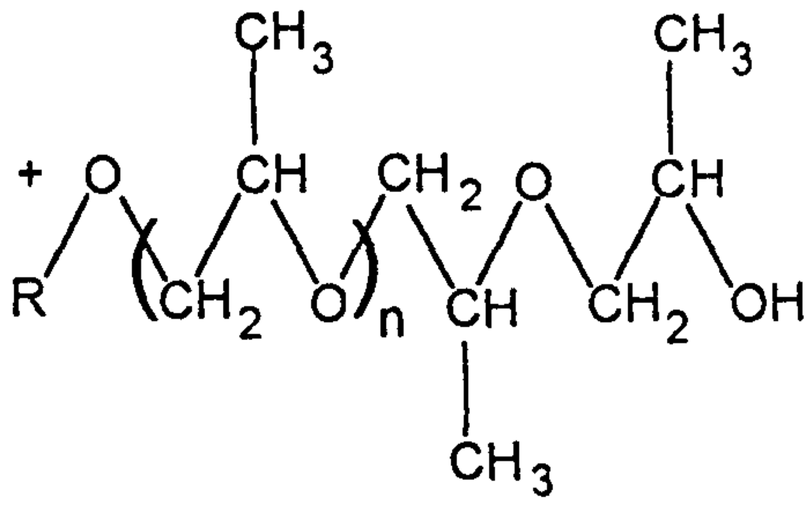
+



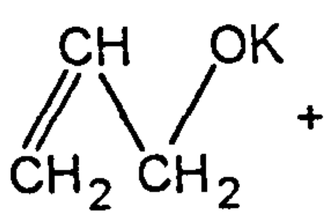


Allyalkoxide

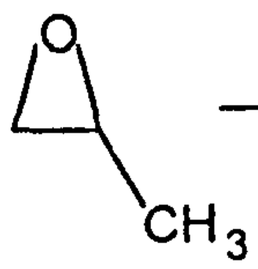
+

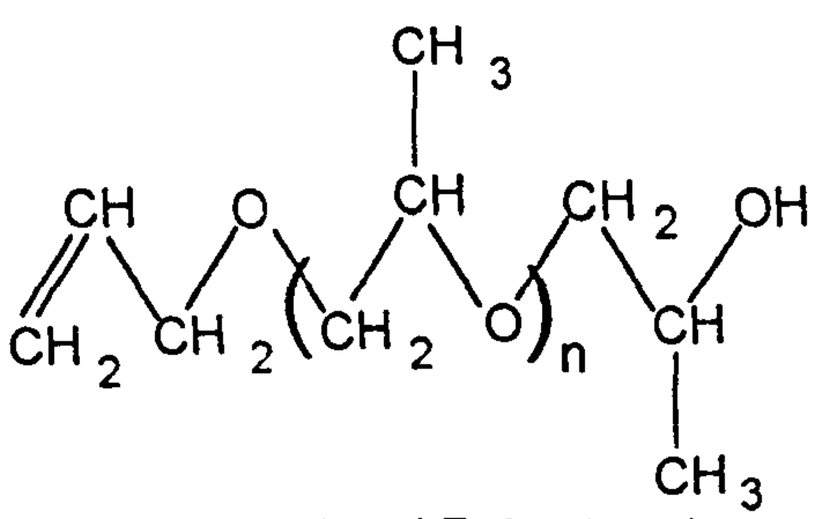


5



+





monofunctional Polyetherol

The water product of reaction 1 is usually removed. Reaction 3 is a proton transfer reaction which is very fast and gives rise to the narrow molecular weight distribution normally seen in commercial polyether polyols. The unsaturated end-group of reaction 5 will not react with isocyanates, although this can be controlled in the final product by reducing the effective functionality of the polyol, but in practice this is only significant for polyols with equivalent weights above 1300. Another reaction which is not shown is the isomerisation of ally alkoxide to propenyl alkoxide. In order to make the polyol in a reasonable time, high temperature and consequently high pressure is required. Upon reaction completion, the catalyst is removed by absorbent treatment followed by filtration or solvent extraction with hexane.

Table 1.1: Common 'starter' materials used in polyol production

Starter	rmm	Starter	rmm
Water*	18.0	Pentaerythritol	136.2
Ethylene glycol*	62.1	Bisphenol A	228.3
Propylene glycol*	76.1	Ethylene diamine	60.1
Dipropylene glycol*	134.2	Toluene diamine	122.2
Glycerol*	92.1	Sorbitol	182.2
Trimethylolpropane*	134.2	Sucrose	342.3

* Substances listed in the UK adhesives list (MAFF project FS2223)[12]

Propylene oxide and propylene glycol and its copolymers with ethylene oxide have by far the largest volume of importance in the polyurethane and surfactant industry compared to all of the other polyepoxides. Products based on polyethers usually have high hydrolytic stability and good low temperature behaviour. However their susceptibility to oxygen and light is a disadvantage especially when used in conjunction with aliphatic polyisocyanates. Polyether diols and triols are preferentially used in the preparation of coatings, sealants and elastomers.

1.4.2 Polyester polyols

Compared to polyethers, polyesters with hydroxyl terminated groups show excellent resistance to light, high temperatures, thermal ageing, resistance to many types of oils and combine high levels of tensile properties with resistance to flexing and abrasion[13]. However they tend to be more expensive and more viscous which makes them harder to handle. They also yield polyurethanes which are more readily hydrolysed, consequently they are only used to make polyurethanes for demanding applications. Typically they are made by the condensation reaction of polyfunctional carboxylic acids (or their derivatives) with polyfunctional alcohols. Common carboxylic acids and glycols are listed in Table 1.2.

Reaction 1.6: Condensation reaction of a difunctional carboxylic acid and diol

$$HOOC\text{-}R\text{-}COOH + HO\text{-}R'\text{-}OH \Leftrightarrow HOOC\text{-}R\text{-}COO\text{-}R'\text{-}OH + H_2O$$

Carboxylic acid diol ester water

This direct esterification is a reversible equilibrium reaction and can only be driven to completion by the continuous removal of the condensation product water (approximately 15% of the total product). Because both the carboxylic acids and the glycols used are polyfunctional the formation of cyclic polyesters is apparent. These low molecular weight oligomers are removed from the final product by vacuum stripping at the end of the reaction. Vacuum stripping is more efficient at higher temperatures but the reaction is restarted and more cyclic species are produced (normally it takes place at approximately 120°C). Hence, this method is not ideal but the final mixture of polyester species cannot easily be purified by recrystallisation or distillation, hence total removal of these oligomers is unlikely. The reaction can be catalysed by acids, bases and transition-metal compounds, however the commercial use of such catalysts is limited due to their undesirable effects on subsequent polyurethane reactions. Another method for the production of polyesters is the reaction of

caprolactone (cyclic ester) with diols to produce polycaprolactone diols used in the manufacture of thermoplastic polyurethane elastomers with improved hydrolytic stability.

Table 1.2: Carboxylic acids and glycols used in the condensation reaction of polyesters

	Carboxylic acids	Formula	rmm
1	Oxalic acid	HOOCCOOH	90.04
2	Succinic acid	$HOOC(CH_2)_2COOH$	118.09
3	Glutaric acid	$HOOC(CH_2)_3COOH$	132.12
4	Adipic acid*	$HOOC(CH_2)_2COOH$	146.14
5	Azelic acid*	$HOOC(CH_2)_7COOH$	188.22
6	Sebacic acid*	$HOOC(CH_2)_8COOH$	202.12
7	Phthalic anhydride*	$C_6H_4(CO)_2O$ *ortho*	148.12
8	Isophthalic acid*	$C_6H_4(COOH)_2$ *meta*	166.13
9	Terephthalic acid*	$C_6H_4(COOH)_2$ *para*	166.13
	Glycols		
10	Ethylene glycol*	$HOCH_2CH_2OH$	62.07
11	Diethylene glycol*	$HOCH_2CH_2OCH_2CH_2OH$	106.12
12	1,2-Propanediol*	$HOCH_2CH(CH_3)OH$	76.10
13	1,4-Butanediol*	$HOCH_2CH_2CH_2CH_2OH$	90.12
14	Neopentyl glycol*	$HOCH_2C(CH_3)_2CH_2OH$	104.15
15	1,6-Hexanediol*	$HO(CH_2)_6OH$	118.18
16	Glycerol*	$HOCH_2CH(OH)CH_2OH$	95.12
17	Trimethylolethane	$CH_3C(CH_2OH)_3$	120.15
18	Trimethylolpropane*	$C_2H_5C(CH_2OH)_3$	134.18
19	Hexanetriol	$HO(CH_2)_4CH(OH)CH_2OH$	134.18

* Substances listed in the UK adhesives list (MAFF project FS2223)[12]

Carboxylic acids (1) to (3) exhibit low stability to hydrolysis. Adipic acid (4) is the carboxylic acid of choice due to its favourable cost/performance ratio, whereas acids (5) and (6) are economically unattractive. The last three acids (7-9) are sometimes added as modifiers. Of the glycols the last four are triols used to introduce branching, the remainder being diols.

Higher triol content in the polyester leads to polyurethanes with greater rigidity, hardness, heat and chemical resistance, as does the introduction of aromatic components. More recently the introduction of the trifunctional castor oil and its derivatives has become apparent as a replacement for polyesters (personal communication). This is a naturally occurring mixture of glyceryl esters in which most of the long fatty acid chains (18 carbon atoms) carry hydroxyl groups (ricinoleic acid). Its average molecular weight is about 940, approximately 70% of which is trifunctional towards isocyanates with the remainder being difunctional. Castor oil imparts excellent water resistance, good weathering resistance, low viscosity to facilitate speed and does not attack inks on the final product.

1.5 ADDITIVES

Additives are added in order to control and modify both the polyurethane reaction itself and the properties of the final polymer. A list of additives used in polyurethane systems are given in Table 1.3.

The first section of the table contains additives usually found in polyurethane adhesive systems, while the lower section is mainly associated with polyurethane foams

Table 1.3: Types of additives used in polyurethane chemistry[4,12,14].

Additive and function	**Type of material and example**
Catalyst - to increase reaction rate	Tertiary amines, Organometallic compounds i.e. dibutyltin dilurate
Cross linking and chain extending agents	Polyols, polyamines i.e. Glycerine triacetate
Antioxidants - to delay degradation by oxidation and thus improve colour stability	i.e. butylhydroxytoluene (BHT)
Heat and chemical stability	Epoxy resins i.e. 2,2-bis(4-hydroxphenyl)propane bis (2,3 epoxypropyl)ether
Chemical resistance	Silanes i.e. Aminopropyltriethoxysilane
Slip agents - for ease of handling	i.e. oleamide and erucamide
Reaction stabilisers	i.e. acetic and phosphoric acid
Blowing agents - to produce foamed structures	water, chlorofluoromethanes and the addition of extra CO_2
Surfactants - to help in foam forming processes	Silicone fluids
Colours	Various pigments, carbon black
Fillers - to modify properties such as stiffness	Particulate inorganic materials
Smoke suppressants - reduce the smoke production on burning	Particulate inorganic/organic materials i.e. polycarboxylates
Flame retardants - to reduce flammability	Phosphorous or halogen containing molecules

There are a number of catalysts available although the Lewis acid dibutyltin dilaurate is preferred mainly because of its low odour in comparison with other catalysts and the small amounts required to achieve high reaction rates.

1.6 POLYURETHANE ADHESIVES IN FOOD PACKAGING

A few decades ago food was sold mainly in bulk containers to the retailer who in turn re-packaged the food into desired quantities at the time of sale. This meant that the nature of the packaging material used was not of paramount importance. However, nowadays food is packaged by the food manufacturer and remains so until consumption by the customer. In choosing a package material for a specific food, both the properties of the material and the requirements of the food have to be considered. The required shelf life of the pack will be obtained only when both sets of properties are compatible under the storage conditions envisaged. A number of plastics are employed as packaging materials. The German Institute for Standardisation[15] term plastics as '*materials, the fundamental components of which consist of those macromolecular organic compounds which are produced synthetically or by modification of naturally occurring products. They are as a rule fusible and malleable under certain conditions (warmth and pressure)*'. These polymers all have different properties with regard to strain potential, stability over a range of temperatures and barrier properties against water, gases, aromas and fats. Due to the many requirements of the foodstuff the plastic is often used in conjunction with other materials such as metal, glass, paper and board, or even other types of polymer. This is to enable the packaging to meet the exact requirements of the food, manufacturers performance and manufacturing needs.

In most cases of film to substrate bonding polyurethane adhesives are used at a coating weight of between 1 and 3 g/m^2. Polyurethane laminated films find applications in the packaging of crisps, nuts, coffee etc., in foods intended to be cooked in its packaging i.e. 'boil in bag' products and those for freezing. One manufacturer estimated that the UK market for food packaging polyurethane adhesives currently stands at about 5,500 tonnes with Europe at about 35,000 tonnes[16]. The lamination of flexible films is the

most important use of polyurethanes in food packaging, but even in this single area there are many different systems in use depending on the application and end bond requirements. For example, flexible laminates for food packaging cover a large spectrum of heat resistance confectionery films through to hot filling and 'boil in bag', to ovenable laminates. The chemical resistance requirements also increase roughly in the same way. At one end of this spectrum thermoplastic adhesives are adequate, whereas cross linked polymers are required for the more demanding applications[17].

Figure 1.1: Common applications of flexible laminate packaging containing polyurethane adhesives, Coffee and Salmon (strong aroma and flavour), boil-in-bag meal and freezer cocktail (high and low temperatures).

An example of such a demanding application is the packaging of frozen kipper fillets, which are intended for storage by freezing then cooked and served directly from the package. Most of these packs are formed by heat sealing and many use a combination of films since one film will not have all the desired properties. The packaging used must withstand both low temperatures and boiling water. It must be non-toxic and impart no odours or flavours to the food. It must provide a barrier to the transmission of water vapour (sometimes oxygen and grease), must be water resistant and capable of being handled on automatic filling and closure equipment. Polyethylene (PE) is a perfect heat sealable flexible film, it has low water permeability but limited air, flavour and odour barrier properties. However polyethylene terephthalate (PET) can overcome these properties and so the two films are bonded together using a polyurethane adhesive.

One advantage of using polyurethane adhesives is their ability to polymerise and form strong bonds without the need for elevated temperatures. The high interfacial bond strengths are derived not just from the physical forces resulting from intimate contact but also from the ability of the polyurethane to form both hydrogen bonds and covalent chemisorption bonds with a range of surfaces. These bonds offer excellent long term durability. It is assumed that this good adhesion can be attributed to the polar nature of the isocyanate group. However when isocyanates alone are used the cured adhesive will be highly cross linked and brittle and thus polyol is added to produce a more elastic cured adhesive[7].

One review[2] has revealed that polyester polyurethanes have emerged as the front runner in adhesives because of their inherently higher cohesive and adhesive properties[18]. Nevertheless poly(ether urethane) adhesive compositions unquestionably have useful adhesive properties[19]. Polyurethane adhesives are produced in three main forms: Solvent based systems, solvent free systems and water based adhesives.

Solvent based systems account for about 47% of the polyurethane adhesives market because of their superior adhesion to difficult surfaces and higher chemical and heat resistance, although this is on the decrease due to environmental concerns in terms of solvent emissions. Solvent based systems offer the best final product control, higher line speeds and thus better productivity. These qualities have brought about the selection of more environmentally friendly solvents and careful choice of dilution parameters for the volatile emissions. In solvent based systems a prepolymer is first made by the addition of the isocyanate to polyol to give an isocyanate terminated prepolymer with an isocyanate value around 3% and a molecular weight between 1000 and 2000. The prepolymer is dissolved in a suitable solvent (usually ethyl acetate or a ketone) to facilitate ease of handling on the machinery. Prior to this application a small amount of polyol is added to initiate the final curing process.

Solvent free adhesive systems have gained a significant share of the film laminating market (over 50%) and still appear to be on the increase. The isocyanate, usually liquid PMDI, and polyol components used in these systems have reduced viscosity and so act as the mobile phase. The relative proportions of these is always in the order 1:1.4, polyol : isocyanate. This excess of isocyanate allows the material to be run on commercial machinery and promotes cross linking within the system. The initial reaction can be delayed by the use of either the uretonimine or the carbodiimide derived from MDI or the more hindered 2,4 MDI based derivatives. The excess of MDI derived components are kept in solution by the addition of stabilisers such as triacetin and triethyl phosphate used as a processing aid. In recent years a great deal of improvements have been achieved with these systems. However there are still restrictions limiting the use of these adhesives - low initial tack, homogeneity of the adhesive mix and variations in the mix ratio resulting in deviating final bonds, relatively slow curing doesn't allow an immediate evaluation of the obtained results. Table 1.4 illustrates the different types of solvent free adhesives available with their advantages and disadvantages.

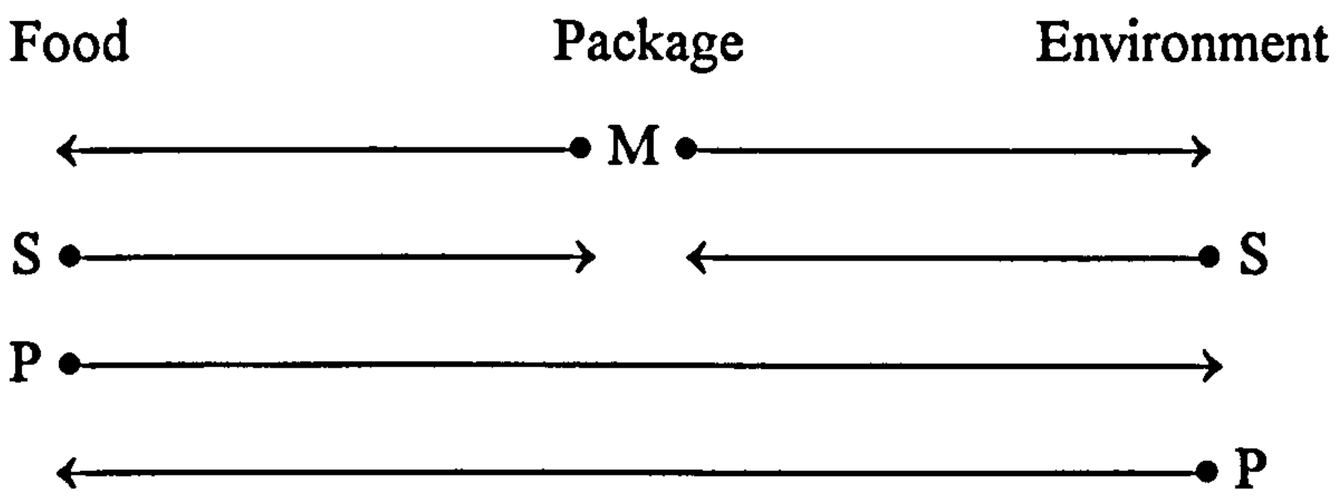
Table 1.4: The advantages and disadvantages of solvent free polyurethane systems on the market[20].

Type of adhesive	Advantages	Disadvantages
1-component, NCO-terminated	-easy handling -good initial tack -good curing in good humidity -low raw material costs	-high processing temperature -isocyanate vapours and aerosol -migration of isocyanate caused by high monomer content -unsafe curing -limited raw material choice
2-component, OH-terminated component and NCO hardener	-fast curing -good bonds by flexible raw material choice -high machine speed	-mixing unit required -low molecular isocyanate as hardener, therefore migration problems
2-component, NCO terminated. with polyol containing hardener	-low amount of isocyanate capable for migration -stoichiometric cross linking	-mixing unit required -migration problems in certain structures
2-component, "monomer-free" NCO terminated, preadduct and polyol hardener	-monomer content < 0.1% -no detectable isocyanate migrantion one day after lamination -high initial tack -suitable for boiling and sterilisation resistant complexes according to BGA/EEC	-processing at elevated temperature -mixing unit required
2-component, OH terminated with "monomer free" aliphatic isocyanate, usually isocyanurates and biurets of HDI and IPDI.	-monomer content < 0.1% -no detectable isocyanate migration one day after lamination -acceptable initial tack -suitable for boiling and sterilisation resistant complexes according to BGA/EEC	-slow reaction -final values partly achieved after storage at elevated temperatures -mixing unit required -higher raw materials costs

Water based polyurethane systems are very rarely used in food packaging applications as they can not withstand high temperatures. They are derived from the reaction products of a diisocyanate and diamine in water. In the first reaction the diisocyanate and polyol are mixed in the ratio of 2:1 respectively, the product of which is then mixed with an amine to give a diamine derivative. Epoxy resins are added to introduce cross linking and acetic acid and surfactants are used to ensure good dispersions in aqueous systems. Water based systems only account for some 2% of the polyurethane adhesives market. Reasons for this level include slow line speeds compared to solvent based systems which are 5 to 10 times faster, slow curing time and poor cured adhesive properties. The environment concerns of volatile emissions in solvent based systems has not even enabled water based systems to gain a foothold in the market and now with the use of more eco-friendly solvents this is set to decrease.

1.7 MIGRATION

Several interactions may occur between food, package and environment[21].



Migration (M) is the transfer of low-molecular weight components from packaging material into the food or the environment. Sorption (S) is the absorption of food components by packaging materials. Permeation (P) is the transfer of components straight through the packaging material. Migration and sorption are diffusion processes, which in polymers is a complex phenomenon. The basic equations governing diffusion processes and hence migration are known as Fick's law.

In general there are three basic mechanisms of migration;

i) No migration in the presence or absence of food.

ii) Migration without the presence of food, although it can be accelerated by some foodstuffs.

iii) Migration dependent on the presence of food, also called leaching which is negligible in the absence of food.

It must be recognised that variations and combinations of these classes are observed. In certain cases migration and sorption may occur which alters the plastic structure and a markedly higher amount of migrating plastic components will be found in the packed product, i.e. HDPE and PP, packaging materials and packed foodstuffs such as pure food fats or other oil releasing products intended for consumption. The free fat / oil penetrates into the plastic and forms a mixed phase (swelling) which steadily continues to expand with increasing duration of contact at the expense of the structurally still unaltered outer area of the plastic packaging material. Through this transformation of deeper layers of the still compact plastic material into a structurally loosened mixed phase, larger amounts of low molecular weight components will be mobilised which due to the many increased diffusion constants, spontaneously migrate from the mixed phase into the fat / oil releasing foodstuff[15].

Potentially any volatile component could be lost by sorption (flavour scalping) to the package. This problem is obvious with plastics, because most flavour components are organic and hence readily soluble in plastics. Migration from plastics is mainly due to: a) residual components and reactants from the manufacturing process, b) Compounds formed during conversion into packaging materials and / or packages, c) Additives incorporated for functionality and d) Adhesives used during conversion. Temperature is probably the most important environmental variable affecting transport processes. Typically acceleration of migration and sorption can be expected at high temperatures[17].

1.8 LEGISLATION

Originally within Europe each country was responsible for ensuring the safety of food packaging to its consumers. This changed in all European Community member states with harmonised legislation in respect to plastic materials and articles intended for use in contact with foodstuffs. The introduction of Directives relating to food packaging are primarily concerned that such materials and articles do not pose a risk to consumer safety. The Directives of relevance for plastics are given in table 1.5. The Commission of the European communities have also published a practical guide for users of these EEC Directives[22], it contains detailed instructions upon how to generate and present the information to be supplied for each evaluation.

Directive 90/128/EEC[23] established a positive list of monomers and other starting substances, an overall migration limit and restrictions on the use of certain substances in the list by setting either a specific migration limit for that substance or limiting the amount of residue of that substance in the finished material, expressed in mg per kg. These limits were determined from a toxicological evaluation of each substance by the EC's Scientific Committee for food. The basic rules for migration testing are given in council Directive 82/711/EEC[24] as amended by Commission Directive 93/8/EEC[25], using suitable food simulants specified in Directive 85/572/EEC[26]. Universal control involves the use of simulants, to overcome the problem of measuring migration from a huge range of different products with an equally wide range of foodstuffs. Additives are listed in Directive 95/3/EEC[27] and 96/11/EEC[28]. These are not positive lists of substances to be used in exclusion of all others, but a 'Scientific Committee for Food approved' list. Other additives for plastics can continue to be used as regulated by national law until the Commission is able to provide a positive list.

Table 1.5: European directives on food contact materials.

Directive	Area of concern
78/142/EEC	concerning the limits for vinyl chloride monomer
80/766/EEC	on determination of vinyl chloride monomer in finished products
81/432/EEC	on the determination of vinyl chloride monomer in foodstuffs
82/711/EEC	on the basic rules for testing migration from plastics
85/572/EEC	on the simulants to be used for testing migration
90/128/EEC	establishing a positive list of monomers and other staring substances
92/39/EEC	1st amendment to Directive 90/128/EEC on plastic monomers
93/8/EEC	1st amendment to Directive 82/711/EEC on testing migration
93/9/EEC	2nd amendment to Directive 90/128/EEC on plastic monomers
95/3/EEC	3rd amendment to Directive 90/128/EEC introduces an incomplete list of additives
96/11/EEC	4th amendment to Directive 90/128/EEC
97/48/EEC	further amendment to Directive 82/711/EEC on testing migration

Adhesives are specifically excluded from the scope of these lists at present but inevitably some of the substances in adhesives are also used in food contact plastics and so are subjected to the above listed controls on plastics. Some of the substances on the European lists of monomers and additives have specific restrictions on toxicological grounds. A number of these compounds are used in the polyurethane industry including isocyanates, which have a general restriction of 1 mg/kg as residue in the finished material. More recently the BGA in Germany have enforced their own isocyanate moiety of 0.2 mg/100cm^3 of suitable food simulant in contact with a surface area of 200 cm^2 contact material. This limit is the limit of detection level of the current analytical method used by industry. A broader regulation encapsulating adhesives in the above directives is the overall migration limit of the finished packaging material, which is 10 mg/dm^2 or 60 mg/kg of the finished article as stipulated in Directive 90/128/EEC.

Future regulatory control of food contact materials will increasingly depend on the use of positive lists of permitted substances supported by migration testing [29,30]. In anticipation of possible future legislation MAFF have funded the compilation of a list of substances used in the manufacture of adhesives for food packaging in the UK, by De Montfort University[12]. The use of a particular monomer or additive in a plastic will therefore be controlled, and the amount that leaches or migrates will also be regulated. The introduction of simulants rather than real foods was proposed a number of years ago before recent improvements in analytical techniques, Recently there has been much debate over this approach particularly as to how well simulants actually do 'simulate' real foods[31]. The simulants currently in use include water, 3% acetic acid, 10% ethanol and olive oil, although much work has been carried out on the use of alternative fatty food simulants rather than olive oil.

Alternative fatty food simulants include 95% ethanol, isooctane and a synthetic triglyceride mixture HB 307, the first three are volatile and thus easier to analyse. In the case of olive oil and HB 307, these fatty food simulants do generate higher results than those encountered using real foods, probably due to the higher fat content which in turn leads to higher fat migration into the packaging and increased diffusion of migrations from the packaging. To correct these higher migration values, Directive 85/572/EEC specifies the use of coefficients to diminish the measured migration values in fatty food simulants and bring them closer to the actual values in the real food.

CHAPTER 2

OVERALL MIGRATION

2.1 INTRODUCTION

Overall migration (global, total migration) is a gravimetric determination based on the simultaneous diffusion of all mobile components (additives, oligomers, monomers etc.) from a plastic packaging material into a contact medium, i.e. a suitable food simulant, under specified conditions of exposure time and temperature. The assessment of overall migration is based upon the weight of the residue remaining after the food simulant, has been removed, typically by evaporation.

In the EEC commission Directive 90/128/EEC an overall migration limit of 10 mg/dm^2 or 60 mg/kg for the finished article is specified. This limit was introduced to control the total amount of substances migrating from a packaging material into food, irrespective of the toxicological significance of these substances, and to reduce the number of specific migration determinations required to ascertain whether the packaging material is fit for use in food contact applications. However since it was first discussed in 1977, this quantification method has come under a lot of criticism[32]. The whole process of overall migration is represented by only one data point and in many instances both the converters and the consumer require more information. The measurement does not provide any information on the nature of the migrants and so is not readily usable from a health and safety view point. Other areas of concern not tackled by this measurement include the maximum possible overall migration at different temperatures, the possibility that migration may be induced by vibration (transport conditions) and ill effects of irradiation. Total migration testing is time consuming and the analytical methods involved, especially in the case of fatty food simulants are sometimes not very accurate and may exhibit poor reproducibility[32].

Commission Directive 82/711/EEC plus amendments in Directive 93/8/EEC set out the basic rules for testing overall migration from plastics. The general method for determining overall migration into volatile food simulants is; A total sample area of 2 dm^2 (10 x 20 cm) is totally immersed in 150 cm^3 of preheated food simulant and stored under various conditions stipulated in commission Directive 85/572/EEC and

dependent on the final application of the contact material. After storage the solvent is decanted off, transferred through a glass filter into a conical flask and rotary evaporated to 25 cm^3. The residue is then dried for 1 hour at 105°C and after cooling is weighed. One limitation of using volatile solvents is the inability to reach high temperatures often experienced during the cooking process (e.g. 175°C).

As olive oil is not volatile the level of overall migration must be determined not from the weight of the residue of the migrated substances in the solvent but from the difference in weight of the sample under study before and after contact with the liquid simulant. For this procedure the sample has to be perfectly conditioned either in a desiccator maintained at c. 50% relative humidity for 24 hours or for moisture sensitive samples by means of vacuum drying at 60°C for 24 hours. This of course is not always possible. Moreover, after storage a certain degree of the oil will be absorbed by the sample and this must be determined. Practical difficulties can arise both in extracting this oil from the sample and quantifying its amount after extraction[33].

This difficulty can be overcome by the use of a volatile solvent[34] as an alternative fatty food simulant, a number of tests comparing olive oil to various solvents found that using isooctane at 20°C for 2 days agreed reasonably with those from the corresponding samples into olive oil for 10 days at 40°C[35]. Hence for these migration studies isooctane was employed as a replacement for olive oil.

A number of other methods have been published for the determination of total migration, these include; The assessment of related parameters by spectrophotometric methodology[36], improved olive oil migration studies using Karl Fishcher titrations[37] and an ultraviolet spectrophotometric method for determining overall migration into fatty food oils[38]. All of these methods boast comparable results with those obtained by traditional methods and reduced analysis times. However to date none have been adopted by the European Committee for Standardisation (CEN).

During this investigation a comparison was made between solid phase extraction and the more traditional evaporation technique for eliminating the volatile food simulants. The latter technique simply relies on heating (approximately 70°C) the volatile food simulant and gently evaporating it off leaving the migration residue for analysis. Solid phase extraction (SPE) is a chromatographic procedure whereby the sample is introduced onto a disposable column or cartridge containing a pre-conditioned sorbent. Any organic matter in the sample is retained in the sorbent while the food simulant is eluted under vacuum. The organic matter from the sample is then eluted and collected using a small amount of organic solvent. A schematic of this apparatus is shown in Figure 2.1.

The sorbent used is commonly a reversed phase material, for example C18 silica, of particle size greater than 40 μm. This packing is held in the cartridge by frits, which are normally of PTFE, polyethylene or stainless steel construction, with a porosity of 10 - 20 μm to offer little flow resistance.

The main steps of SPE used in this context are:

1, Conditioning the packing.
2, Sample application.
3, Washing the packing.
4, Recovery of the analyte.

The cartridge is first conditioned to remove any impurities and allow the sorbent to be solvated. The sample is then aspirated at between 2 and 6 cm^3/min. Washing the cartridge ensures that any inorganic material which may be present in the sample is eluted before the analyte is recovered using an organic solvent such as methanol or acetonitrile.

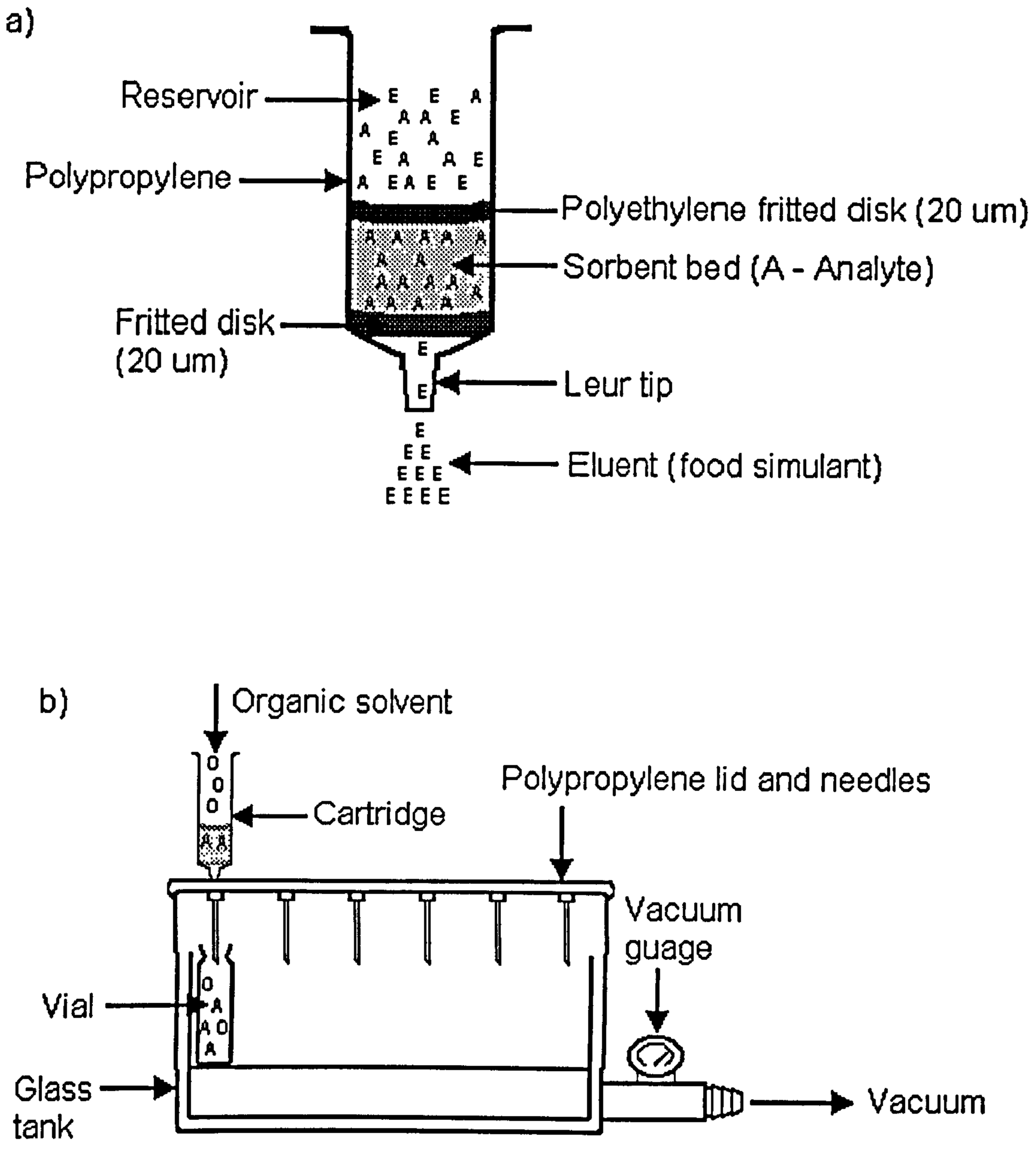


Figure 2.1: Schematic of SPE apparatus, a) SPE cartridge and b) multi-position SPE vacuum manifold.

The advantages of this type of system is that by the use of a multi-position manifold, a number of samples can be concentrated simultaneously, resulting in faster analysis. The recovery of the analyte in methanol or acetonitrile leads to easier and faster evaporation compared to residues in water. A possible disadvantage of this technique is the relative cost of the cartridges as they should be discarded after each run. It should be noted that SPE concentration could only be carried out on samples using either water or 3% acetic acid as food simulants because both ethanol and isooctane would interfere with the retention of the migrants by the sorbent.

In plastic food contact materials overall migration testing is a well established method. In this work it was applied as an initial surveillance technique both to confirm compliance with EC limits and to become familiar with the samples and equipment used. However, by quantifying the overall migration of these commercial samples comparisons can also be made with further more complex analytical techniques used to quantify specific migration levels. Hence the overall migration level is the sum of all migrating species;

i.e. $O = I + P + A$ where O = Overall migration
I = Isocyanate migration
P = Polyol migration
A = Additive migration

This equation can be used to check the complex quantification methods applied and to assess the level of migrants not specifically detected.

2.2 EXPERIMENTAL

2.2.1 Reagents

Millipore water (18MΩ)

HPLC grade Methanol and Ethanol

Glacial acetic acid

(Fisher Scientific, Loughborough, Leicestershire, UK)

HPLC grade 2,2,4-Trimethylpentane (*isooctane*)

(Sigma-aldrich, Gillingham, Dorset, UK)

2.2.2 Apparatus

GC oven - Carlo Erba GC 8000

Mettler AE 100 4 figure balance

Techelut 12 position vacuum manifold

Techelut SPE C18 1000 mg/6 cm^3 cartridges

(HPLC Technology, Macclesfield, Cheshire, UK)

EDM6 Edwards high vacuum pump

(BOC Ltd, Crawley, UK)

Hulme Martin dual electronic heat sealer

(Hulme Martin Ltd, London, UK)

2.2.3 Samples

Overall migration studies were carried out on the following commercial laminate samples:

Table 2.1 Commercial laminate samples tested for overall migration.

Code	Configuration	Polyurethane
Sample 1	60 μm LDPE / PU / 12 μm PET	2.4 g/m^2 Polyether
Sample 2	75 μm LLDPE / PU / 12 μm MET PET (2g/m^2 PVDC)	2.5 g/m^2 Polyether
Sample 3	45 μm (75:25 LDPE:BLLDPE) / PU / 12 μm PET	1 - 1.5 g/m^2 Polyester
Sample 4	50 μm LDPE / PU / 7 μm ALU / PET	1.5 g/m^2 Polyester
Sample 5	50 μm Curex LDPE / PU / 7 μm ALU / PET	1.5 g/m^2 Polyester
Sample Z	70 μm LDPE / PU / 12 μm PET	Polyether
Sample 481	70 μm LDPE / PU / 12 μm PET	Polyether
Sample 484	70 μm LDPE / PU / 12 μm PET	Polyether

All of the above samples except sample 2 were bonded using solvent free polyurethane adhesives.

2.2.4 Migration into aqueous food simulants

The different aqueous simulants were held in pouches (20 cm x 20 cm) prepared by heat sealing individual sheets of the laminate samples. The pouches plus contents were maintained at 70°C for 2 hours after which the contents were removed, evaporated to dryness and the residues weighed. Two methods of achieving dryness were employed evaporation at 70°C and solid phase extraction using Techelut C18 1000 mg/6 cm^3 cartridges.

In the evaporation method the exposed simulant was removed from the pouch and placed in a pre-weighed vial which was left in the oven at 70°C until total dryness was obtained. The vial was then heated to 105°C for 1 hour, allowed to cool and weighed.

The SPE method of concentration was carried out as follows; The cartridges were pre-conditioned using two 10 cm^3 aliquots of methanol and washed with two 10 cm^3 aliquots of water. The sample was then aspirated at 4 cm^3/min followed by two 10 cm^3 aliquots of water to wash the cartridge, which was then dried under vacuum for 1 minute. A pre-weighed vial was then placed under the cartridge to catch the two 10 cm^3 aliquots of methanol eluted down the column to remove the retained components from the pouch extract. This methanol was dried off in the oven at 70°C and the residue was then heated to 105°C for 1 hour, cooled and weighed. All the samples were heated at 105°C for 1 hour, cooled and weighed a number of times to achieve constant weight.

2.2.5 Migration into Isooctane

20 cm x 20 cm (4 dm^2) chopped samples and 2 x 20 cm x 20 cm (8 dm^2) pouches of commercial laminate and their component films were prepared and exposed to 100 cm^3 isooctane. These tests were carried out either in a round bottom flask (chopped samples) in which case both sides of the laminate and the edge of the adhesive layer were exposed to the simulant. After 2 days at 20°C the simulant was removed from the laminate/film and taken to dryness by evaporation at 60°C. The residue was then heated to 105°C for 1 hour before the overall migration was determined.

2.3 RESULTS

All the overall migration data given corresponds to pouch sizes of 20 x 20 cm (8 dm^2) and 4 dm^2 chopped samples. In all cases for each concentration method, migration testing was carried out simultaneously to ensure any variation in the data was not a result of differences in sample age. This is especially important as the polyurethane adhesive is a reactive system and hence possible migrant levels will differ with age.

Table 2.2: Comparison of the overall migration from commercial laminate pouches into water, using concentration by evaporation at 70°C or solid phase extraction.

Sample	Evaporation method (mg/ dm^2)	SPE method (mg/ dm^2)
Blank water	0.063 ± 0.000	0.069 ± 0.006
PE film pouch	0.081 ± 0.006	0.063 ± 0.001
Sample 1 pouch	0.100 ± 0.009	0.163 ± 0.018
Sample 2 pouch	0.113 ± 0.013	0.106 ± 0.010
Sample 3 pouch	0.063 ± 0.004	0.063 ± 0.000
Sample 4 pouch	0.063 ± 0.004	0.075 ± 0.006
Sample 5 pouch	0.049 ± 0.004	0.056 ± 0.006
Sample Z pouch	0.063 ± 0.005	0.037 ± 0.007
Sample 481 pouch	0.025 ± 0.000	0.029 ± 0.004
Sample 484 pouch	0.100 ± 0.003	0.067 ± 0.000

Table 2.2 outlines the migration levels into water. The final migration residues from tests using this simulant have provided good samples for further analysis by other techniques covered later in this work. Hence migration testing into water as the food simulant provides the bulk of the data for no other reason than for use in further analysis. However this simulant is also the suggested replacement for the majority of food types listed in the commission Directive 85/572/EEC.

Table 2.3: Comparison of the overall migration from commercial laminate pouches into 3% acetic acid, using concentration by evaporation at 70°C or solid phase extraction

Sample	Evaporation method (mg/dm^2)	SPE method (mg/dm^2)
Blank 3% acetic acid	0.125 ± 0.000	0.125 ± 0.000
PE film pouch	0.088 ± 0.005	0.131 ± 0.006
Sample 1 pouch	0.125 ± 0.000	0.144 ± 0.006
Sample 2 pouch	0.113 ± 0.013	0.113 ± 0.003
Sample 3 pouch	0.138 ± 0.006	0.156 ± 0.006
Sample 4 pouch	0.169 ± 0.019	0.172 ± 0.010
Sample 5 pouch	0.138 ± 0.006	0.131 ± 0.006

Table 2.3 shows the overall migration of commercial laminate samples into 3% acetic acid. This simulant is generally used for laminates intended to be in contact with acidic foodstuffs usually with a pH of 4.5 or less, for example fruit chunks and fermented milk products such as yoghurt, buttermilk and products in association with fruit.

Table 2.4: Overall migration from commercial laminate pouches into 10% ethanol, using evaporation at 70°C as the concentration step.

Sample	Overall Migration (mg/ dm^2)
Blank	0.038 ± 0.000
PE film pouch	0.088 ± 0.001
Sample 1 pouch	0.150 ± 0.006
Sample 2 pouch	0.100 ± 0.010
Sample 3 pouch	0.163 ± 0.003
Sample 4 pouch	0.163 ± 0.013
Sample 5 pouch	0.150 ± 0.0038

Overall migration into 10% ethanol would be used for laminates intended to come into contact with foodstuffs containing alcohol like wines and spirits. In the Directive 85/572/EEC this simulant appears to be the least suggested simulant for testing plastics, but this is not unexpected as to date most alcoholic beverages are stored in glass rather than plastic. However new products are now on the market, such as alcoholic cocktails served in laminate pouches and suitable for home freezing.

Table 2.5: Overall migration from commercial laminate pouches and chopped samples into isooctane, concentrated by evaporation at 60°C.

Sample	Migration (mg/dm^2)			
	pouch film	pouch laminate	chopped films	chopped laminate
Blank isooctane	0.000	0.000	0.000	0.000
Sample 1	0.813	2.363 ± 0.138	1.950	2.625
Sample 2	0.813	1.925 ± 0.175	1.525	2.600
Sample 3	1.275	1.438 ± 0.108	0.925	1.475
Sample 4		1.500 ± 0.125	0.525	1.475
Sample 5		1.481 ± 0.147	1.125	1.025

For samples 4 and 5 no films were provided to make pouches from and in the case of chopped films the edges of the laminate not bonded were used. The use of fatty food simulants in the Directive are quite common since many foods contain some level of fat.

2.4 DISCUSSION

The highest migration levels for the pouched laminates were found when isooctane was used as the food simulant (Table 2.5) (between 11 and 19 mg from 8 dm^2 of laminate). Aqueous 3% acetic acid and 10% ethanol produced very similar results (between 0.9 and 1.3 mg from 8 dm^2 laminate). The migration into water ranged from 0.2 to 1.3 mg from 8 dm^2 laminate pouch. All of these fall well within the total migration limit of 10 mg/dm^2. However it must be noted that these levels were determined several months after lamination when possible migrants may have further reacted with the reactive polyurethane system or have been lost during the long storage period. The results within each food simulant are comparable from laminate to laminate, probably due to the use of polyethylene as the inner layer in all cases.

Overall migration into water shows the lowest levels, with 3 % acetic acid and 10% ethanol being slightly higher. Isooctane migration may be higher due to its ability to penetrate into the polyolefin film and act as a plasticiser. One drawback of using isooctane as an alternative fatty food simulant is its application to plastic materials which may be subjected to elevated cooking temperatures. Since it is volatile it is not a suitable alternative simulant for tests which require high temperatures, for example for foods which will be cooked in the oven at high temperatures.

In most sample cases the end application of the commercial laminate was unknown and so overall migration tests were carried out using all of the simulants, although normally the end application of the laminate would be known and the appropriate simulant could be selected accordingly. Similarly the contact time of the simulant and the plastic could not be calculated from the final application estimated contact time, specified in Directive 85/572/EEC and so the conditions of 2 hours at 70°C were adopted.

Solid phase extraction proved a faster method of concentrating the migrants than evaporation and the levels obtained suggest the methods are comparable. However it must be remembered that the SPE method could only be applied to the migration tests into water and 3% acetic acid, as both 10% ethanol and isooctane would interfere with the cartridge sorbent.

Previous work in this area by Lawson and Barkby[39] provides global migration data for comparison. Their results range from 0.1 to 4.2 mg/dm^2 in aqueous food simulants compared to 0.02 to 1.9 mg/dm^2 and 4.1 to 20 mg/dm^2 in olive oil compared to 1.4 to 2.6 mg/dm^2 in isooctane. In most cases the published results are five times greater than those obtained in this work. The reason for this difference in total migration is due to the films incorporated in the laminates. In both the published work and these investigations polyethylene film was used as the inner layer but in the previous work, nylon is the outer layer. This alone gives migration data of between 2.0 and 7.5 mg/dm^2 in aqueous food simulants, due to the presence of caprolactam and its low molecular weight oligomers migrating out of the film. In these investigations the laminates used were composed of polyethylene film and either PET or slight variations of PET, none of which show much potential for migration. Hence it is not unexpected that the previous results are higher as a proportion of the migrants will be caprolactam based species from the nylon film.

CHAPTER 3

ANALYSIS OF THE DIISOCYANATE COMPONENT

3.1 INTRODUCTION

Due to the toxicity of the diisocyanate component and its hydrolysis product, the diamine, the levels of residues in polyurethane systems used in food packaging require close monitoring to ensure possible exposure is kept to a minimum. This is reflected in the European Commission Directive 90/128/EEC, where a specific migration limit of 1 mg/kg of NCO in the finished article, is promulgated. This low value for the residue and the nature of the isocyanate component has resulted in the publication of a number of different methods for the quantification of isocyanates. Early methods were concerned with the detection of isocyanates in the atmosphere to maintain safe working conditions during manufacture[40]. In 1957 Marcali[41] developed a quantitative colorimetric method for the determination of isocyanates in air, by hydrolysing the isocyanate to give its corresponding amine and coupling it to produce an azo dye. This method can only be applied to the analysis of primary aromatic isocyanates, for example MDA from MDI used in adhesives and TDA from TDI used in adhesives and foams. Methods of isocyanate detection in air can be adopted to the determination of levels in laminate extracts as in both cases samples are in the liquid phase before derivatisation, although sample collection varies. The first paper concerned with the determination of isocyanate levels in laminates described an HPLC method for the determination of toluene diamine (TDA) in aqueous extracts of food contact boil-in-bag and retortable pouches[42].

Due to the reactive nature of the isocyanate group it is specifically reacted to give a more stable compound, either by hydrolysis to the corresponding amine or by derivatisation to enable better detection. These derivatising agents include; N-4-nitrobenzyl -N-n-propylamine[43,44], dibutylamine (DBA)[45] and 9-(methlaminomethyl) anthracene (MAMA)[46]. The latter derivatising agent MAMA can be used with reverse phase HPLC for the determination of ten different isocyanates in polyurethane articles and laminates intended for food use. Developed by Damant et al[46] in 1995, this method was then adopted by the European Committee for Standardisation (CEN) in September 1998.

One problem with this method is that under the analytical procedure specified polymeric isocyanate components are not detected even though both monomeric and polymeric isocyanates are used in the manufacture of polyurethane adhesives for laminated food packaging. EU legislation calls for a maximum level of residual NCO moiety and the above test would therefore appear to exclude part of the species it is supposed to be measuring.

One reported method for the detection of polymeric isocyanates is a size exclusion chromatography technique for the determination of polymethylene polyphenylene isocyanate (polymeric MDI) again in air. It was developed by Beasley and Warner[44] in 1984 and uses N-(p-nitrobenzyl)-N-n-propylamine as an in situ derivatising agent. Another type of polymeric isocyanate used in the manufacture of polyurethane adhesives is a pre-polymer. Here the isocyanate is first reacted with a small amount of a high molecular weight polyol (Mwt 2000) to produce a long chain polymer with isocyanate functionality at both ends for further reaction with a lower molecular weight polyol (Mwt 400) immediately before lamination. It is doubtful whether any residual prepolymer based NCO moiety would be detected by the CEN test. One possible advantage of the CEN method is that it detects the NCO moiety by direct derivatisation rather than the Marcali method which relies first on hydrolysis and then derivatisation. Hydrolysis by airborne moisture to produce MDA can take place at any time after the liquid adhesive has been spread on the film. Measurement based on determination of NCO as the $-NH_2$ group might therefore be expected to yield high readings in this respect.

Polyurethanes are reactive systems and curing can proceed for a number of days after lamination. During lamination the two components are thoroughly mixed before application to the plastic film. In the initial mixture the isocyanate component is added in excess to facilitate ease of handling and spreading by maintaining the mixture in the liquid phase for a prolonged length of time. This excess isocyanate then reacts over a number of days to a negligible level, but initially the amount of free isocyanate is not at an acceptable

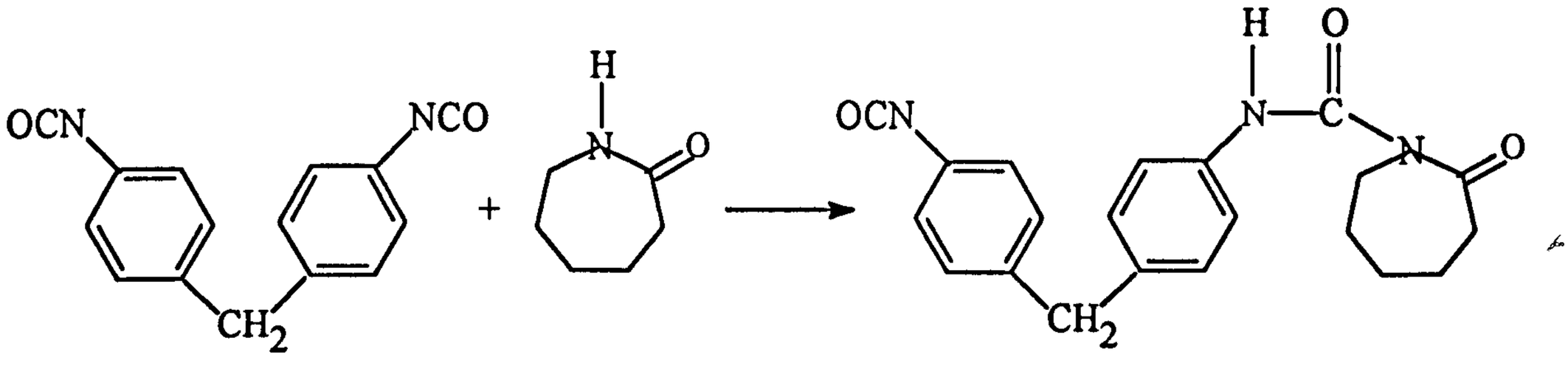
level for use in contact with foodstuffs. The Flexible Packaging Association (FPA) recognise this problem and recommend a delay time between lamination and dispatch to the customer. This delay period is four days for solvent based polyurethane systems and seven days for solvent free polyurethane systems. This difference in delay times between solvent based and solvent free systems is due to the higher isocyanate content in solvent free systems, acting as a carrier during lamination, compared to solvent based systems where ethyl acetate is the carrier.

The storage of laminates for up to a week after lamination can cause a number of problems for the converter and customer; the need for storage space prior to dispatch, and the timely and sometimes costly delay of urgent orders. One way of combating this problem is the use of Curex®. Curex® is brand new technology introduced and patented by Novacote International of Hamburg[47]. It offers ultra fast curing properties as well as faster aromatic amine decay, thus it acts as an accelerator.

1 - 2% of Curex® is added to the lamination film during film blowing or the film manufacturing process. The advantage of introducing this additive via the lamination film and not to the wet adhesive samples is to maintain a long 'pot-life', ideally of 30 - 40 minutes. The pot-life of the adhesive is very important from the converter's point of view. It is the length of time the adhesive is mixed before it starts to cure and becomes unsuitable for processing by the lamination machinery. Having a long pot-life often results in a long curing time and a short pot-life means a short curing time. Hence, converters prefer a short curing time, but this comes hand in hand with a short, often unacceptable, pot-life which can lead to an uncontrolled application weight. The curing time can be reduced by the addition of the accelerator in the film without affecting the pot-life of the adhesive.

Curex® is based on ε-caprolactam and its low molecular weight oligomers and acts as a kind of catalyst increasing the degree of cross linking and detectable amine decay. It is stated by Novacote that it can reduce curing times from days to hours which in turn reduces the level of diamine free to migrate, and combined with special Novacote adhesives can offer UV-curing speeds. The reaction of these cyclic amides with isocyanates results in the formation of acyl urea.

Reaction 3.1: Chemistry of the action of ε-caprolactam as a catalyst for MDI based polyurethane curing.



Isocyanate (MDI) e-caprolactam acyl urea (tertiary amine)

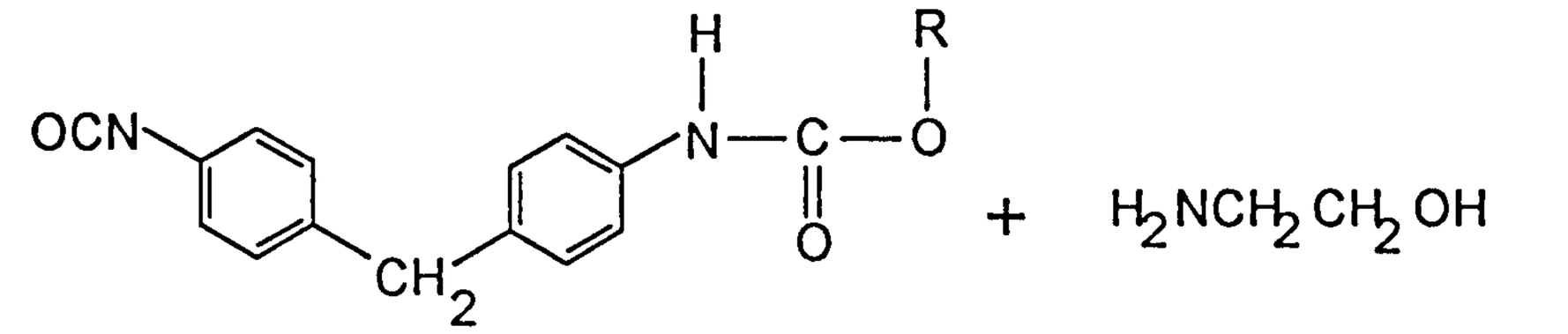
This reaction reduces the amount of residual isocyanate available to react with water. The cyclic-acyl urea now contains another NCO group for further reaction, and the extended size of the isocyanate will lead to cross linking. The high level of intermolecular hydrogen bonding, a dominant characteristic of caprolactam; may act as the driving force of the urea-polyol formation and thus increasing the curing speed. However, in this case the caprolactam is not acting as a catalyst and would be included in the final polyurethane network.

It is important to monitor the level of migratable isocyanates in commercial laminates and although the CEN method stipulates using HPLC with fluorescence detection, the lack of this type of analytical equipment has led industry to adopt a similar colorimetric method to that first reported by Marcali. A similar method has also been adopted by De Montfort University as it determines both the monomeric and polymeric primary aromatic amines. Since MDI and its derivatives are the most popular isocyanate used in polyurethane adhesives for use in food packaging in the UK and the only type of isocyanate encountered in this investigation, this method seems most appropriate.

As previously shown the isocyanate component can be either MDI or more commonly one of its derivatives, such derivatives include polymeric MDI and MDI prepolymers. None of these derivatives are detected using the CEN method and although the Marcali test can detect the amine groups it cannot provide any information on the nature of the species. If the isocyanate component is a prepolymer, one way to investigate its make-up is to break its urethane bonds and analyse each resulting component. Hydrolysis[48], glycolysis[49,50,51] and aminolysis are well known chemical processes for the decomposition of polyurethane systems to low molecular weight products. Glycolysis is the preferred method of decomposition as it is faster. In these investigations glycolysis was the chosen method of decomposition using ethanolamine, the reaction of which is given in reaction 3.2.

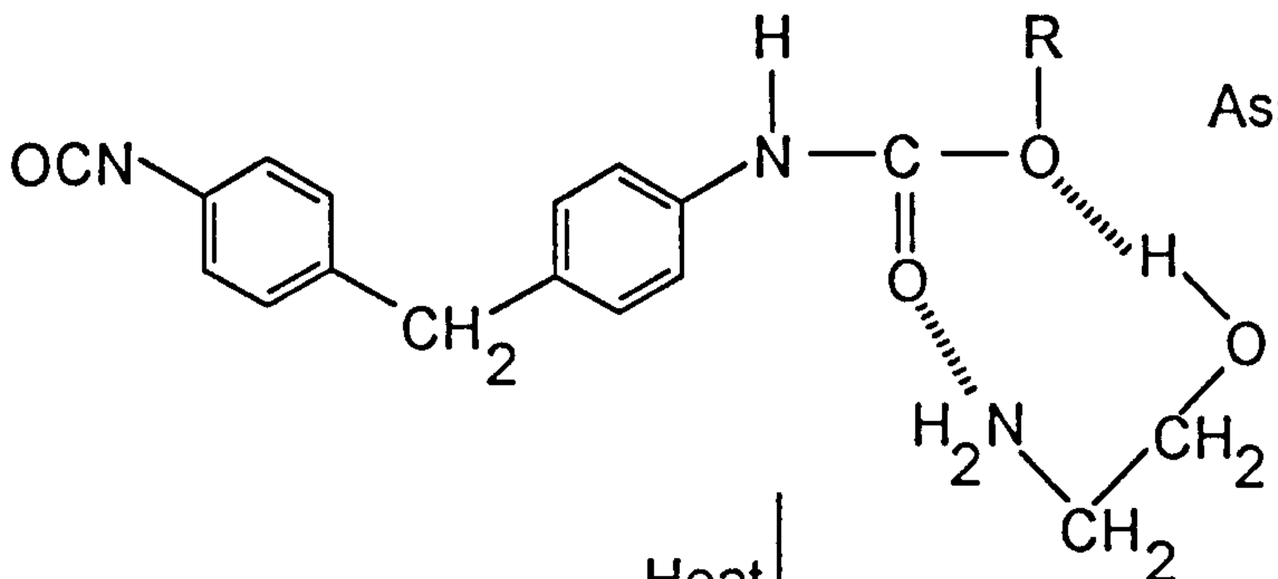
The ethanolamine used for this decomposition is an alkanolamine and hence it contains both a hydroxyl and an amine group and so in theory this decomposition could be either glycolysis or aminolysis. However, Kanaya and Takahashi[49] used gel permeation chromatography and ^{13}C-NMR to monitor all of the reaction products and intermediates and from these results concluded that glycolysis was taking place.

Reaction 3.2 Decomposition of an MDI based urethane by glycolysis using ethanolamine



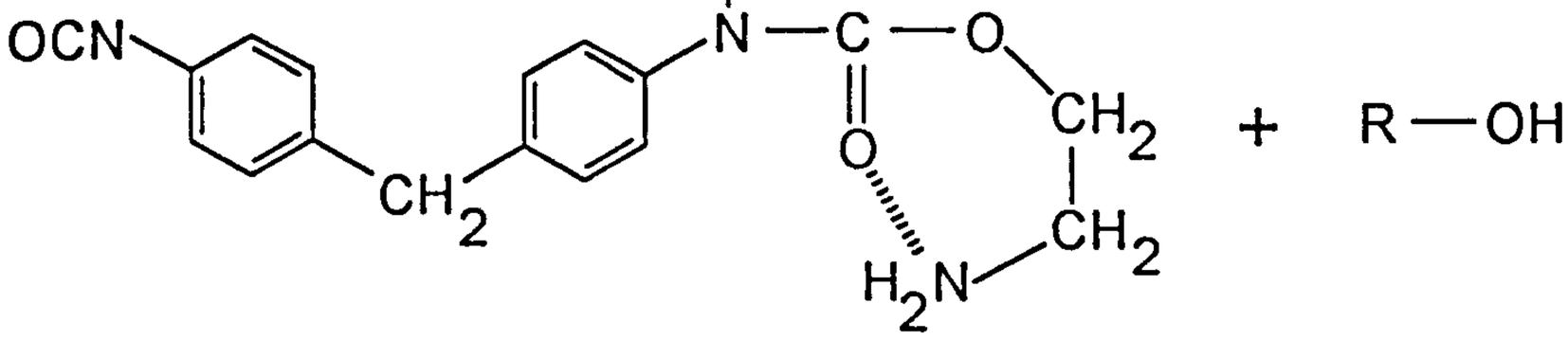
MDI Urethane

Ethanolamine (MEA)



Association of urethane and MEA

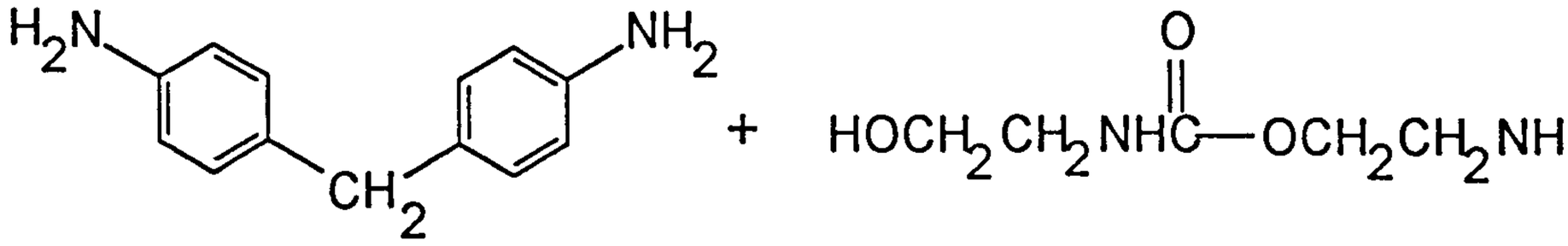
Heat



MDI-MEA urethane adduct

polyether

Decomposition by MEA



MDA

2-hydroxyethylcarbamic acid 2-aminoethylester (HECE)

To date this method has only been applied to MDI and polyether based polyurethane foams, the decomposition of which produces two layers: a clear top layer containing the pure polyether and a yellow bottom layer containing MDA and 2-hydroxyethyl carbamic acid ester prepared from the glycolysis products during the decomposition reaction. Hence, if after the decomposition of the cured isocyanate component two distinct layers are visible in the reaction product then this indicates the presence of a polyether in the sample and thus that the isocyanate component is a prepolymer.

Initial investigations were carried out to determine the migratable amine levels from a number of commercially available laminates using a colorimetric method similar to that first developed by Marcali. One method developed at De Montfort University using rotary evaporation to concentrate the samples and the other a method developed by industry incorporating solid phase extraction as the concentration technique. Where possible when the laminates were received early enough amine decay curves were constructed to show the rate of amine decay and the curing time for a variety of commercial laminates. The CEN test was carried out on a number of samples courtesy of the Central Science Laboratory (CSL) in Norwich using HPLC analysis and fluorescence detection.

Following the determination of the diamine levels and the rate of amine decay the isocyanate component was de-formulated to establish the nature of the diamine and hence isocyanate group. The isocyanate components were subjected to glycolysis to separate the prepolymer which was then qualitatively analysed by Matrix Assisted Laser Desorption/Ionisation (MALDI) mass spectroscopy to identify the nature of the prepolymer.

3.2 EXPERIMENTAL

3.2.1 Reagents

Millipore water (18MΩ)

HPLC grade glacial acetic acid, hydrochloric acid and methanol

AR grade acetone

N-(1-naphthyl) ethylene diamine dihydrochloride (NEDD)

4,4'-methylene dianiline (MDA)

Aniline hydrochloride

(Fisher Scientific, Loughborough, Leicestershire, UK)

Ethanolamine, Gentisic acid, Sodium nitrite

(Sigma-Aldrich, Gillingham, Dorset, UK)

Ammonium sulphamate

(Merck/BDH, Lutterworth, Leicestershire, UK)

3.2.2 Apparatus

Hulme Martin heat sealer - dual electronic

(Hulme - Martin Ltd, London, UK)

EDM6 Edwards vacuum pump

(BOC Ltd, Crawley, UK)

Unicam UV-2-100 UV/VIS spectrometer

(Unicam, Cambridge, Cambridgeshire, UK)

Techelut 12 position vacuum manifold

Techelut SPE C18 100 mg/6 cm^3 cartridges

(HPLC Technology, Macclesfield, Cheshire, UK)

Finnigan Lasermat 2000 MALDI-MS

(Thermabio Analysis, Ashford, Middlesex, UK)

3.2.3 Samples

The nature of the commercial laminates investigated are outlined in table 3.1.

Table 3.1: Composition of the commercial laminates analysed for isocyanate content.

Code	Composite films	Polyurethane	Coating weight
Sample 1	60μm LDPE / PU / 12μm PET	Solvent free, polyether	2.4 g/m^2
Sample 2	75μm LLDPE / PU / 12μm MET PET (2 g/m^2 PVDC)	Solvent based, polyester	2.5 g/m^2
Sample 3	45μm (75:25 LDPE : BLLDPE) / PU / 12μm PET	Solvent free, polyester	1 - 1.5 g/m^2
Sample 4	50μm LDPE / PU / 7μm ALU / 12μm PET	Solvent free, polyester	1.5 g/m^2
Sample 5	50μm LDPE (Curex) / PU / 7μm ALU / 12μm PET	Solvent free, polyester	1.5 g/m^2
Sample 6	45μm (75:25 LDPE : BLLDPE) / PU / 12μm PET	Solvent free, polyester	1 - 1.5 g/m^2
Sample TC2	45μm PE / PU / 12μm PET	Solvent based, 1 component	2.6 g/m^2
Sample TC3	45μm PE / PU / 12μm PET	Solvent based, 2 component	2.6 g/m^2

3.2.4 Colorimetric Determination of Primary Aromatic Amines

Solutions :- Acid solution - 0.3M acetic acid, 0.5M hydrochloric acid

Sodium nitrite - 0.25 g in 50 cm^3 water

Ammonium sulphamate - 2.5 g in 100 cm^3 water

Coupling reagent - N(1-Napthyl) ethylene diamine dihydrochloride - 0.5 g in 50 cm^3 water

4,4'-methylene dianiline (MDA) - 50 µg in 100 cm^3 water

Aniline hydrochloride - 50 µg in 100 cm^3 water

3.2.4.1 In-house method

8 dm^2 sample pouches (20 cm x 20 cm) were prepared, each containing 100 cm^2 of the chosen food simulant (either water or 3% acetic acid in water) and 4 dm^2 laminate samples were chopped up into 1 cm squares and placed in a round bottom flask containing 100 cm^3 of the food simulant. These samples were then extracted by heating for either 2 hours at 70°C or refluxed at 100°C for one hour respectively. After extraction the aqueous food simulant was decanted off from the residue film and rotary evaporated under vacuum at 60°C to 10 cm^3. The derivatisation step was then carried out using the solutions specified in section 3.2.4 as follows:- 5 cm^3 of acid solution and 2 cm^3 acetone were added to the concentrated simulant, 1 cm^3 sodium nitrite solution was added and left for 10 minutes. After this, 2 cm^3 ammonium sulphamate solution was introduced and left to react for a further 10 minutes, then 2 cm^3 coupling reagent was added and the colour allowed to develop for one hour before measurement of colour intensity at 550 nm.

3.2.4.2 Industrial method[52]

Industry recommend placing 2.5 dm^2 of test sample into a cell with 125 cm^3 of simulant for 2 hours at 70°C. However as this method is to be compared to that already carried out at DMU 8 dm^2 pouches were prepared containing 100 cm^3 of simulant and heated for 2 hours at 70°C. After migration of the amine into the relevant food simulant under realistic conditions, the aqueous food simulant was decanted off from the residue film and the derivatisation step carried out using the solution concentrations stipulated in section 3.2.4:-

12.5 cm^3 of 1M hydrochloric acid and 2.5 cm^3 sodium nitrite were added and left for 10 minutes before the addition of 5 cm^3 ammonium sulphamate. This was shaken and left for 10 minutes to react, 5 cm^3 N(1-napthyl) ethylene diamine dihydrochloride was added and left for two hours to allow the colour to develop. The coloured product was then concentrated using solid phase extraction columns (Techelut C18 1000 mg/6 cm^3) and a vacuum manifold column processor. The column was conditioned using 12 cm^3 methanol followed by 12 cm^3 80:20 methanol : 0.5M hydrochloric acid and 12 cm^3 0.1M hydrochloric acid. The sample was aspirated at 4 cm^3/min and rinsed using 12 cm^3 0.1M hydrochloric acid. The column was then dried for one minute before eluting with 10 cm^3 80:20 methanol : 0.5M hydrochloric acid which was made up to 20 cm^3 for measurement at 550 nm.

Calibrations were plotted from a number of MDA and aniline hydrochloride standards, prepared from stock solutions, ranging from 0.0 to 5.0 μg in 10 cm^3 water before undergoing the derivatisation step either by the in-house or industrial method.

3.2.4.3 Isocyanate determination by the Central Science Laboratory

A number of samples of both commercial laminates and wet isocyanate pre-polymers were sent to the Central Science Laboratory (CSL) in Norwich, for the analysis of extractable monomeric isocyanates rather than total amine (aka total isocyanate) using HPLC and MAMA derivatisation[46].

3.2.4.4 De-formulation of Isocyanate component pre-polymer

Samples of the wet isocyanate component were spread on aluminium foil and left to completely cure over a number of weeks. 5 g of the cured component was then removed from the foil and placed in 50 cm^3 ethanolamine. This was then refluxed at 150°C for 3 hours and allowed to cool. Where an isocyanate component is a pre-polymer the isocyanate and polyol are separated by glycolysis and the polyol forms a layer on top of the ethanolamine which contains the isocyanate derivatives. These layers were then decanted off, diluted in acetonitrile and analysed by MALDI-MS to determine both the nature of the polyol and isocyanate used.

3.3 RESULTS

3.3.1 Colorimetric determination of primary aromatic amines

The colorimetric Marcali method for the determination of primary aromatic amines relies on the Beer-Lambert law of light absorption. This deals with the influence upon the relative proportion of the light absorbed by a sample, of a) sample thickness (Lambert law) and b) sample concentration (Beer law). Hence if the sample thickness remains constant then the sample absorbance is directly proportional to the sample concentration. The law is expressed by the relation:

$$A = \varepsilon c l$$

where A = Absorbance

ε = Molar absorptivity / extinction coefficient (mole/litres cm)

c = Concentration (mole/litre)

l = Path length of light through sample (cm)

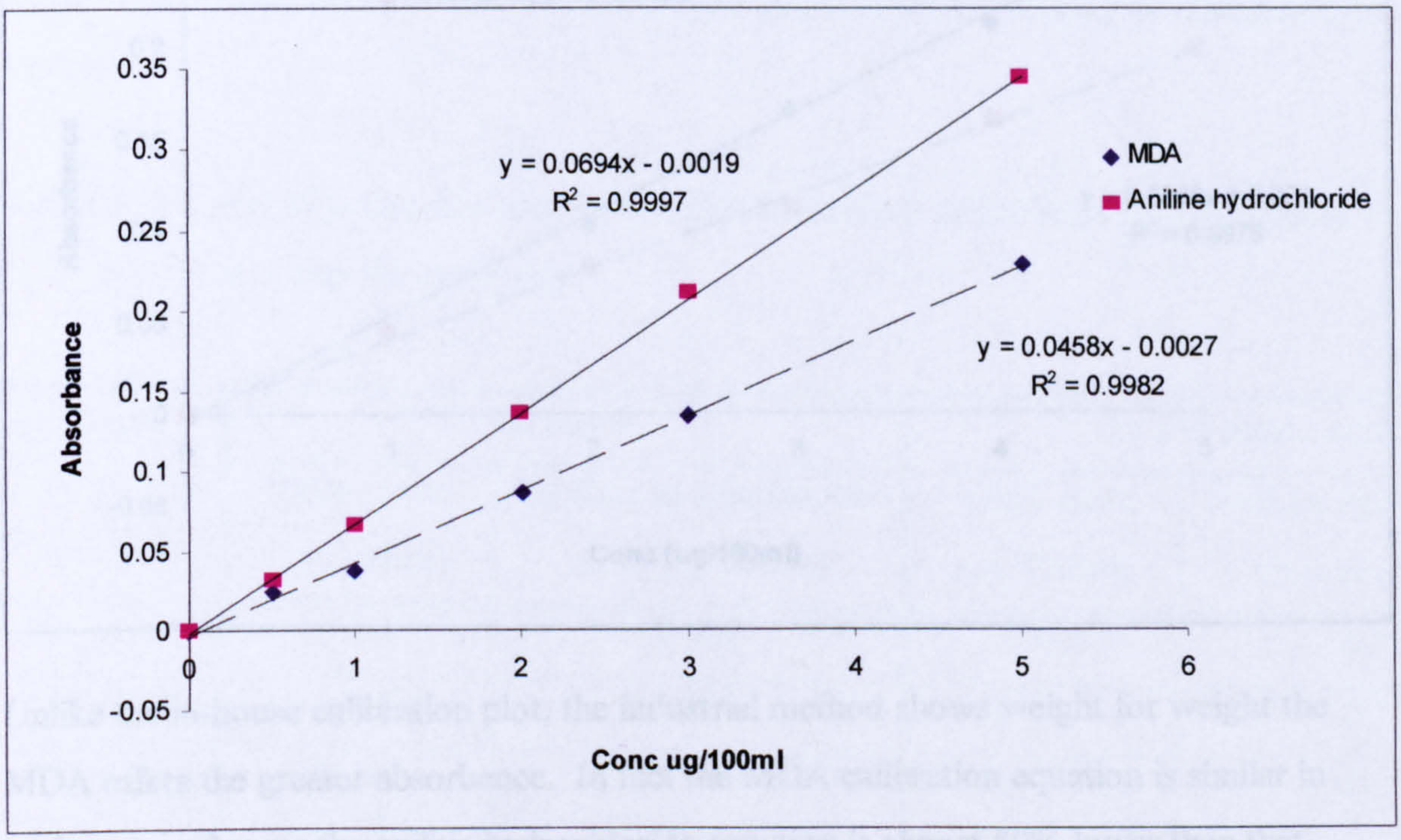
The extinction coefficient is a molecular property, characteristic of the absorbing species, dependent upon the wavenumber of absorption but not on the concentration of the species or the path length.

3.3.1.1 Calibration of MDA and aniline hydrochloride

A calibration curve must be plotted before a relationship between the absorbance and concentration can be established. Industrial methods incorporate aniline hydrochloride for this in order to avoid using more hazardous MDA. A number of MDA and aniline hydrochloride standards were prepared and their absorbance were plotted against concentration to provide linear calibration plots for use in determining the migratable

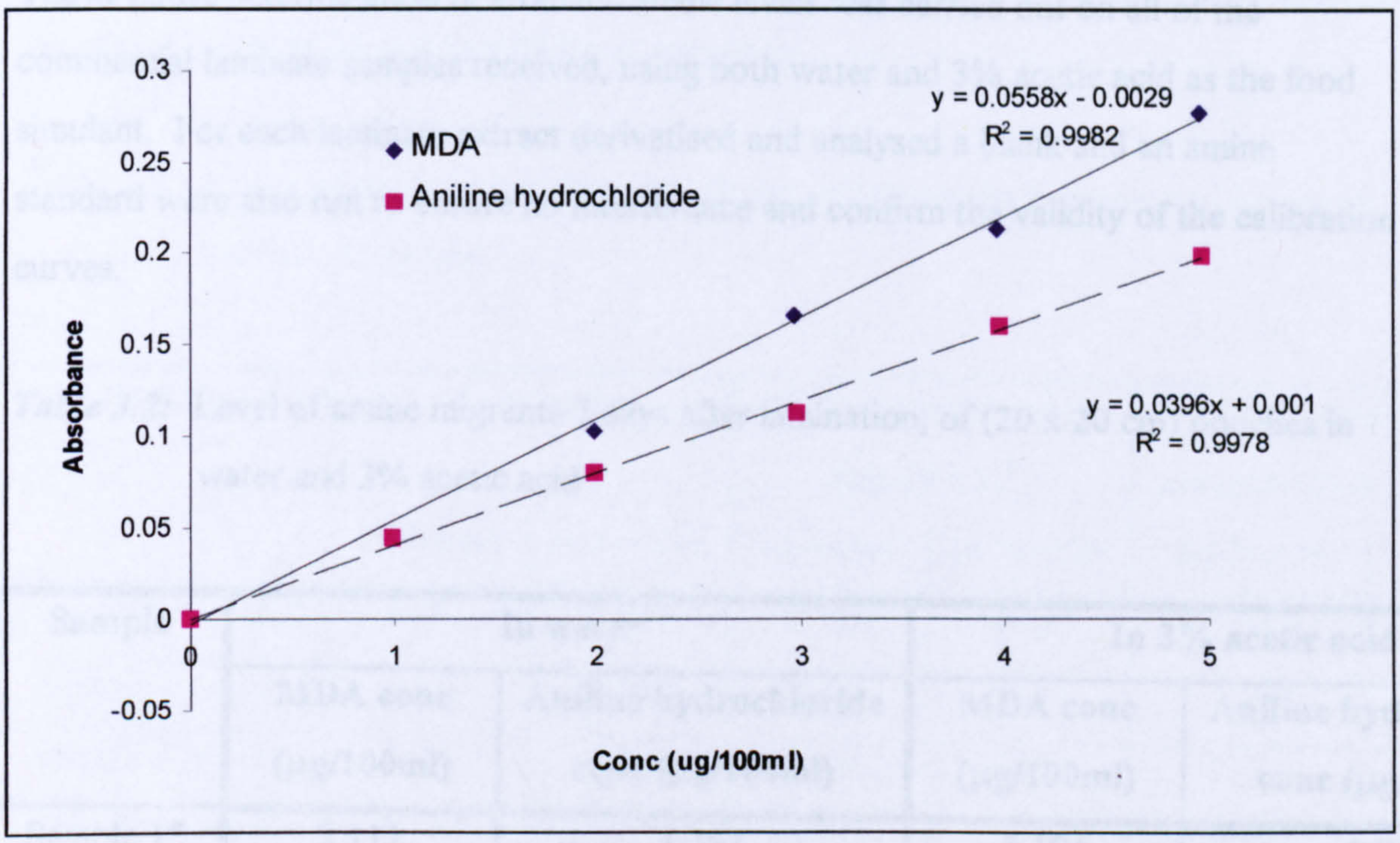
amine content of commercial laminate samples. Calibration curves were calculated using both the in-house and industrial methods of derivatisation. All readings were taken at 550 nm using 4 cm quartz cells.

Figure 3.1: In-house calibration of MDA and aniline hydrochloride standards in 100 cm^3 water



The extinction coeffiecient of both MDA and aniline hydrochloride are comparable. However this is on a mole to mole basis, due to the differences in molecular weight on a weight for weight basis the aniline hydrochloride displays a greater absorbance due to higher molar content. This finding was unexpected due to the functionality of these compounds. One mole of MDA containes two functional groups compared to aniline hydrochloride which contains one. This indicates that the functionality of the primary aromatic amine does not dictate the relative absorbance of the compound.

Figure 3.2: Industrial calibration of MDA and aniline hydrochloride standards in 100 cm^3 water



Unlike the in-house calibration plot, the industrial method shows weight for weight the MDA offers the greater absorbance. In fact the MDA calibration equation is similar in both cases, whereas the aniline hydrochloride equation is almost 50% lower than that observed in the in-house calibration. The molar extinction coefficients for this calibration should be comparable to that of the in-house plot, however the aniline hydrochloride value is approximately 50% of that calculated from the MDA equation. This value appears to be more in keeping with the relative functionality of the two compounds.

It seems more realistic to use MDA as the calibration standard as this is in most cases the actual amine detected in commercial laminates, and there are no interferences within both method work ups apparent for MDA and hence the methods appear to be comparable for MDA alone.

3.3.1.2 Primary aromatic amine levels in commercial laminate samples

The in-house determination of aromatic amine levels was carried out on all of the commercial laminate samples received, using both water and 3% acetic acid as the food simulant. For each laminate extract derivatised and analysed a blank and an amine standard were also run to ensure no interference and confirm the validity of the calibration curves.

Table 3.2: Level of amine migrants 7 days after lamination, of (20 x 20 cm) pouches in water and 3% acetic acid

Sample	In water		In 3% acetic acid	
	MDA conc (µg/100ml)	Aniline hydrochloride conc (µg/100ml)	MDA conc (µg/100ml)	Aniline hydrochloride conc (µg/100ml)
Sample 1*	2.111	1.382	1.194	0.777
Sample 2	0.408	0.258	0.496	0.316
Sample 3	72.068	47.549	137.876	90.978
Sample 4	120.562	80.070	187.655	124.638
Sample 5	57.785	38.370	97.286	64.609
Sample 6	39.032	25.748	68.006	44.869
TC2	0.996	0.834	5.658	4.530
TC3	0.576	0.502	2.718	2.198

* 77 days after lamination

Samples 3, 4, 5 and 6 give exceptionally high results, above the specific migration limit promulgated by the European Union. In the case of sample 3 the manufacturer speculated that the elevated values may be the result of dispatch immediately after curing and

consequent storage at low temperatures preventing complete curing. Hence an identical sample (6) was dispatched 7 days after lamination for comparison.

The in-house and industrial colorimetric methods were then run in parallel on commercial laminate samples in 3% acetic acid for comparison.

Table 3.3: Amine levels migrating from pouch samples using the in-house and industrial methods in parallel.

Sample	Absorbance		MDA concentration ($\mu g/100cm^3$)		Aniline hydrochloride concentration ($\mu g/100cm^3$)	
	In-house	Industrial	In-house	Industrial	In-house	Industrial
2 $\mu g/100cm^3$ MDA	0.101	0.032	2.136	0.625		
Sample 4 pouch	0.259	0.143	5.456	2.615	4.344	3.586
Sample 4 pouch	0.373	0.170	7.851	3.098	6.241	4.268
Sample 5 pouch	0.286	0.171	6.023	3.116	4.794	4.293
Sample 5 pouch	0.330	0.138	6.947	2.525	5.526	3.459
Sample 3 pouch	0.327	0.224	6.889	4.066	5.476	5.631
Sample 3 pouch	0.410	0.193	8.628	3.511	6.857	4.848

The in-house method gives the greater absorbances and these are approximately double in most cases. This is reflected in the MDA concentrations as the calibration equations are similar. In the case of aniline hydrochloride levels are more comparable to each other, due to the differences in calibration equations.

Two commercial laminate samples were received on the day of lamination (TC2 and TC3). A portion of each sample was placed in an air tight jar containing silica jel, at ambient temperature in the laboratory, while the other portion was exposed to normal laboratory conditions. After 70 days of storage the amine levels were determined in both sample portions, as pouches containing 3% acetic acid and water. Migration and detection was carried out as outlined in section 3.2.4.1, and the results are shown below.

Table 3.4: Amine (MDA) levels 70 days after lamination of laminate pouches in water and acetic acid, after normal and dry storage.

Sample	Storage condition	MDA conc (μg/100cm^3)
TC2 in water	Normal	0.3510
TC2 in water	Dry	0.7080
TC2 in 3% acetic acid	Normal	0.3930
TC2 in 3% acetic acid	Dry	0.5820
TC3 in water	Normal	0.0357
TC3 in water	Dry	0.4768
TC3 in 3% acetic acid	Normal	0.3718
TC3 in 3% acetic acid	Dry	0.7289

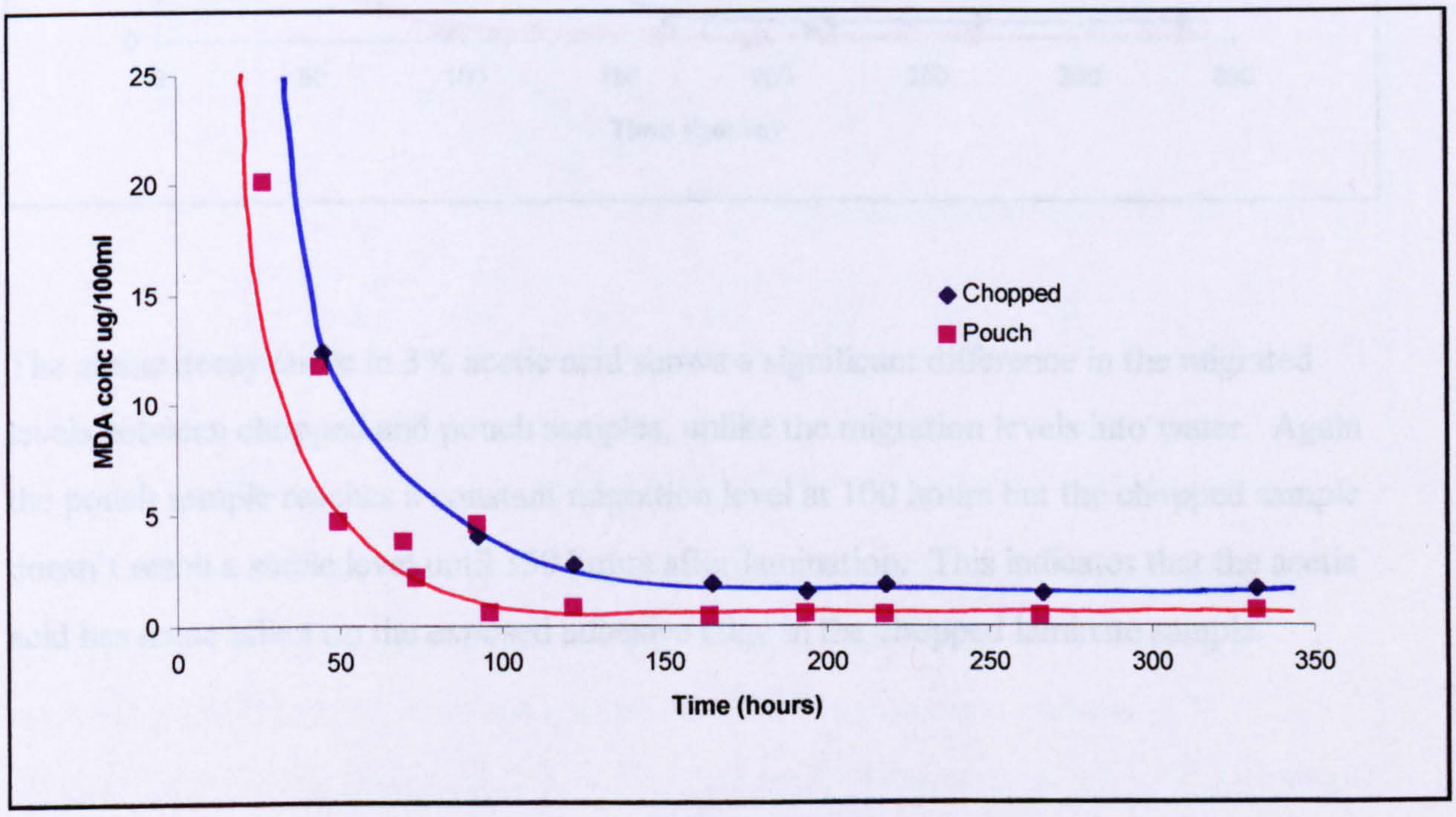
The results shows a higher migration level in the laminate stored under dry conditions, almost a 2 fold increase in most cases, this indicates the importance of atmospheric water in the curing process.

3.3.1.3 Primary aromatic amine decay after lamination

Where commercial laminate samples were received within a few days of lamination, a number of laminate extractions were carried out to obtain an overall picture of the amine/isocyanate depletion as a function of time following the lamination process.

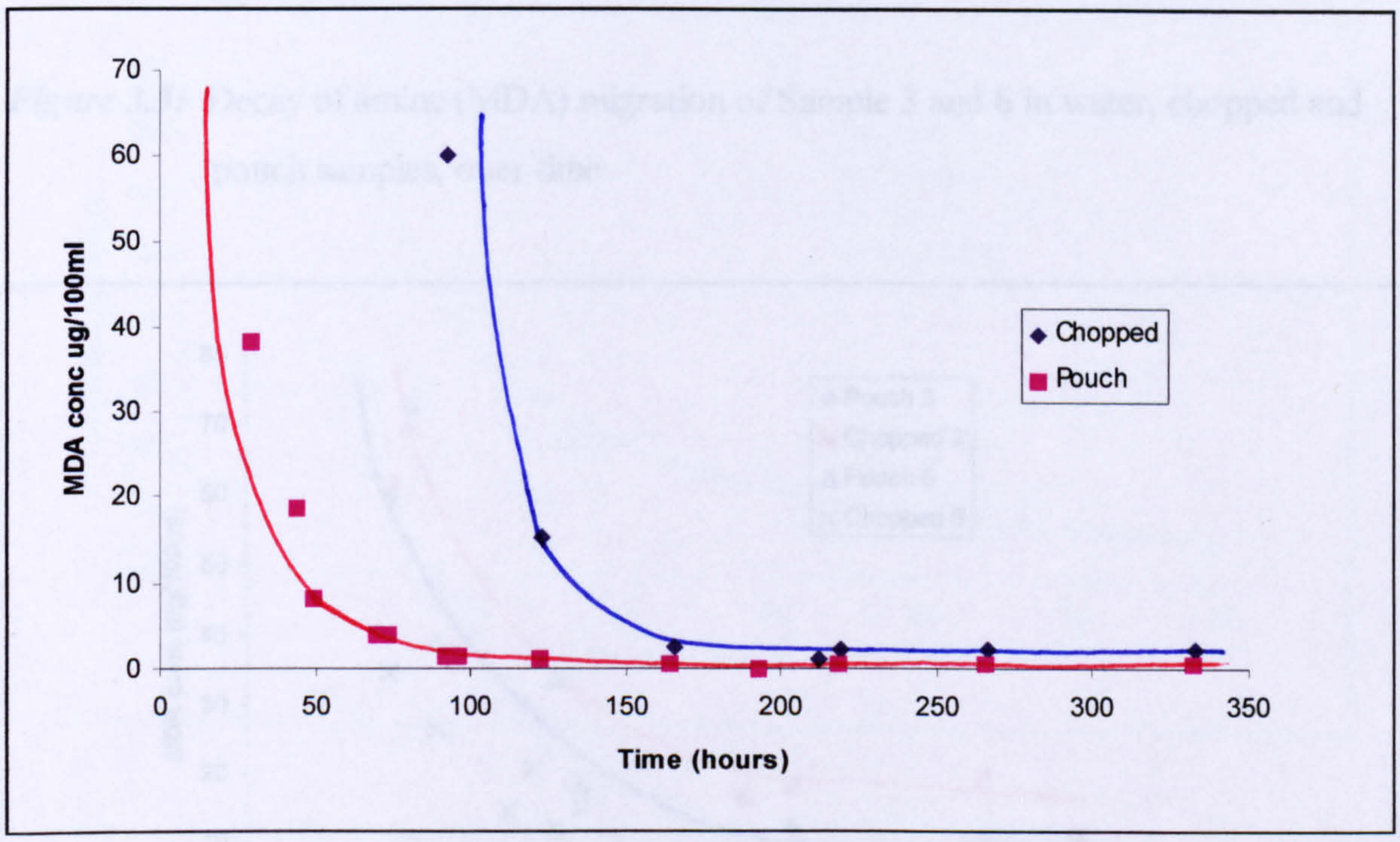
Sample 2 was received within 24 hours of lamination so a number of Marcali tests were carried out on both pouch and chopped samples to establish an amine decay curve

Figure 3.3: Decay of amine (MDA) migration of sample 2 into water, chopped and pouch samples, over time.



This graph initially shows a rapid drop in the level of migrating amine until a constant level is reached after approximately 100 hours (4 days). Results for the chopped and the pouch sample show similar levels of migratable primary aromatic amine.

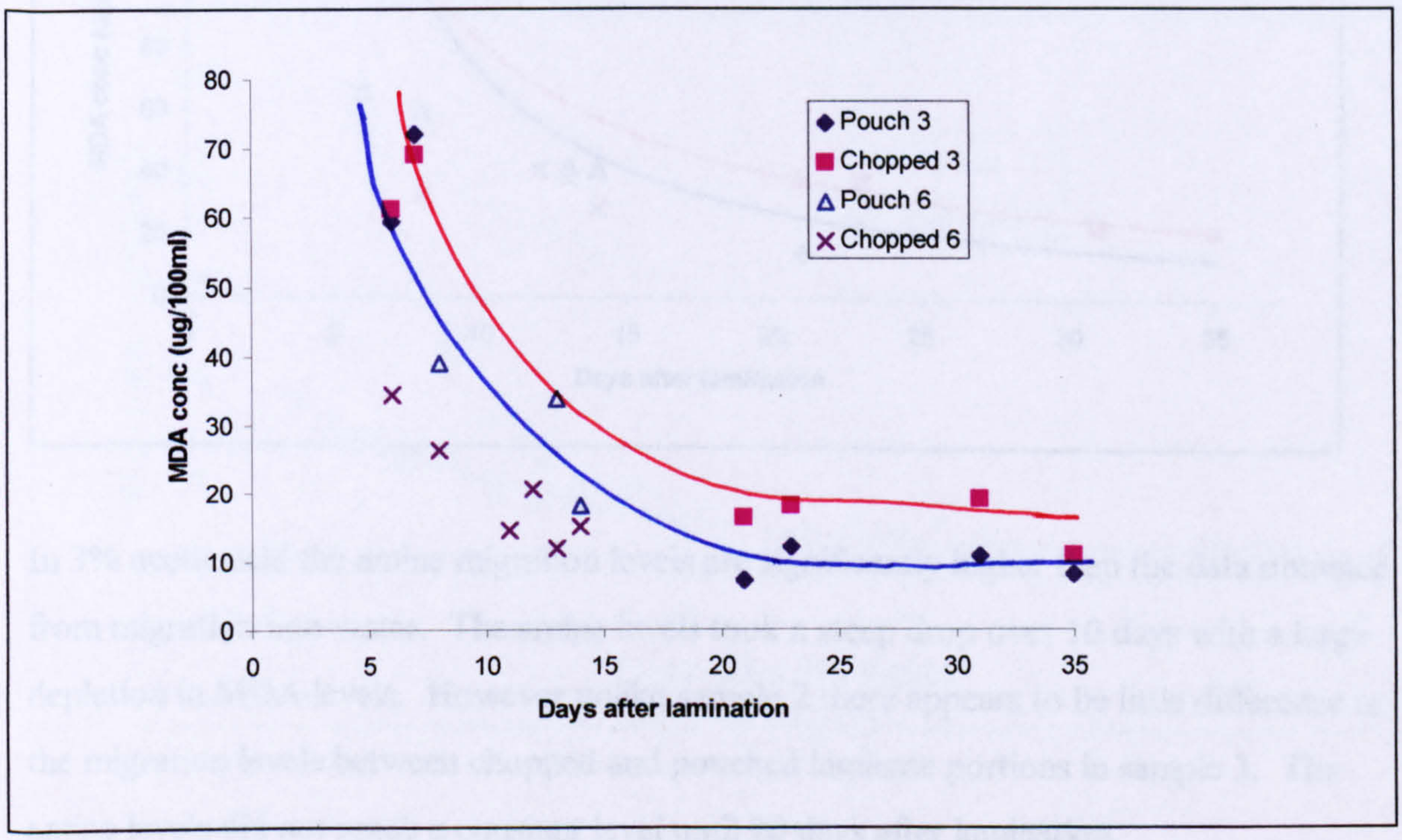
Figure 3.4: Decay of amine (MDA) migration of Sample 2 into 3% Acetic acid, chopped and pouch samples, over time



The amine decay curve in 3% acetic acid shows a significant difference in the migrated levels between chopped and pouch samples, unlike the migration levels into water. Again the pouch sample reaches a constant migration level at 100 hours but the chopped sample doesn't reach a stable level until 150 hours after lamination. This indicates that the acetic acid has some effect on the exposed adhesive edge in the chopped laminate sample.

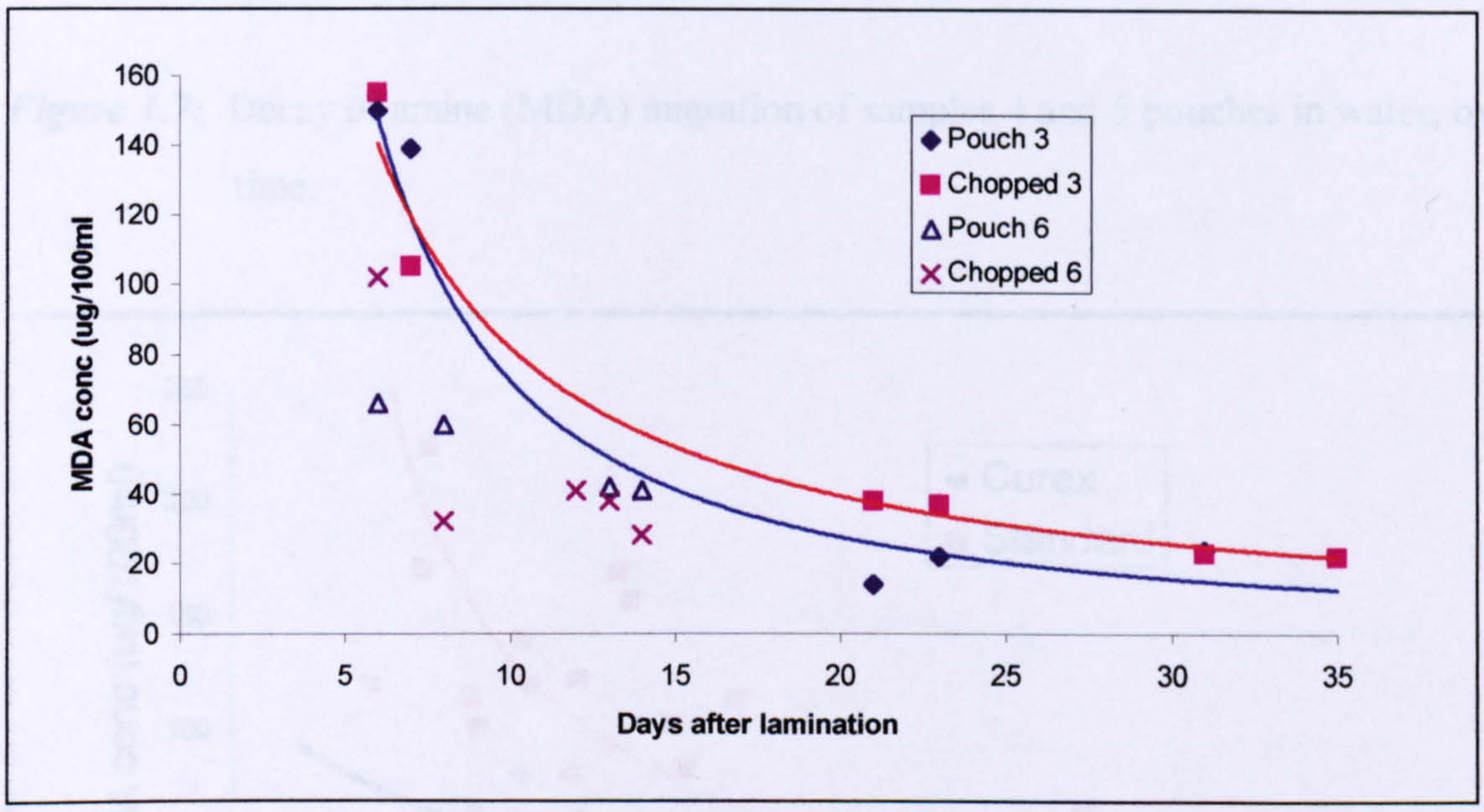
Sample 3 arrived one week after lamination. Initially one extract was taken as it was believed that initial decay would have taken place. However the migratable amine level was still high and so an amine decay curve was constructed.

Figure 3.5: Decay of amine (MDA) migration of Sample 3 and 6 in water, chopped and pouch samples, over time



The elevated amine levels observed in sample 3 led to the analysis of another identical sample (6). The amine decay curve in water shows a shallow curve not reaching a constant until 15 days after lamination and the data from sample 6 appears to be comparable with that from sample 3. To test the method employed at DMU these samples were sent for HPLC analysis to CSL in Norwich.

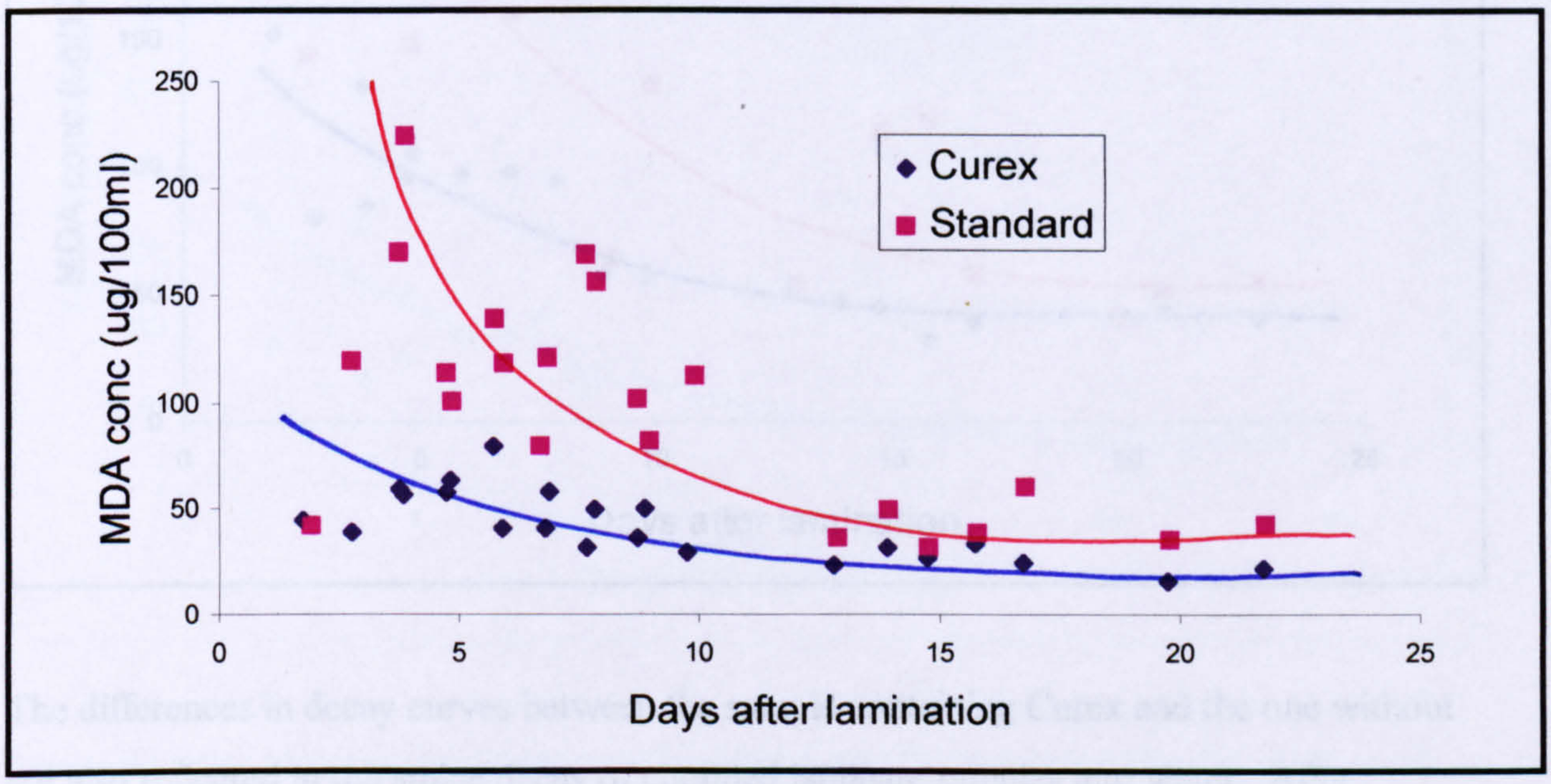
Figure 3.6: Amine (MDA) decay of Sample 3 in 3% Acetic acid, chopped and pouch samples, over time.



In 3% acetic acid the amine migration levels are significantly higher than the data obtained from migration into water. The amine levels took a steep drop over 10 days with a large depletion in MDA levels. However unlike sample 2 there appears to be little difference in the migration levels between chopped and pouched laminate portions in sample 3. The amine levels did not reach a constant level until 20 days after lamination.

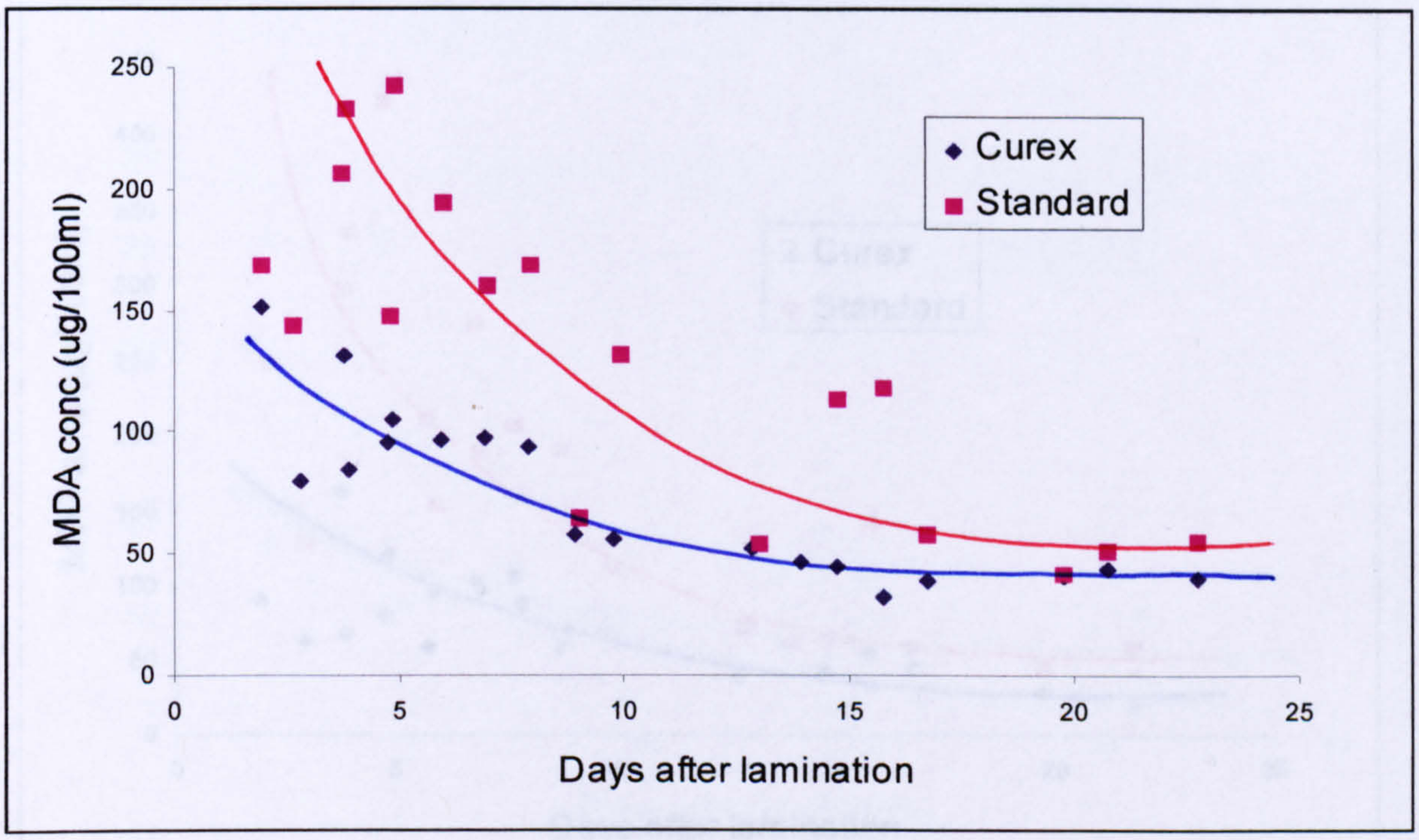
Samples 4 and 5 contain the same polyurethane adhesive system. However one laminate (Sample 5) contains Curex in its polyethylene layer, a caprolactam based product used to accelerate the curing process.

Figure 3.7: Decay of amine (MDA) migration of samples 4 and 5 pouches in water, over time.



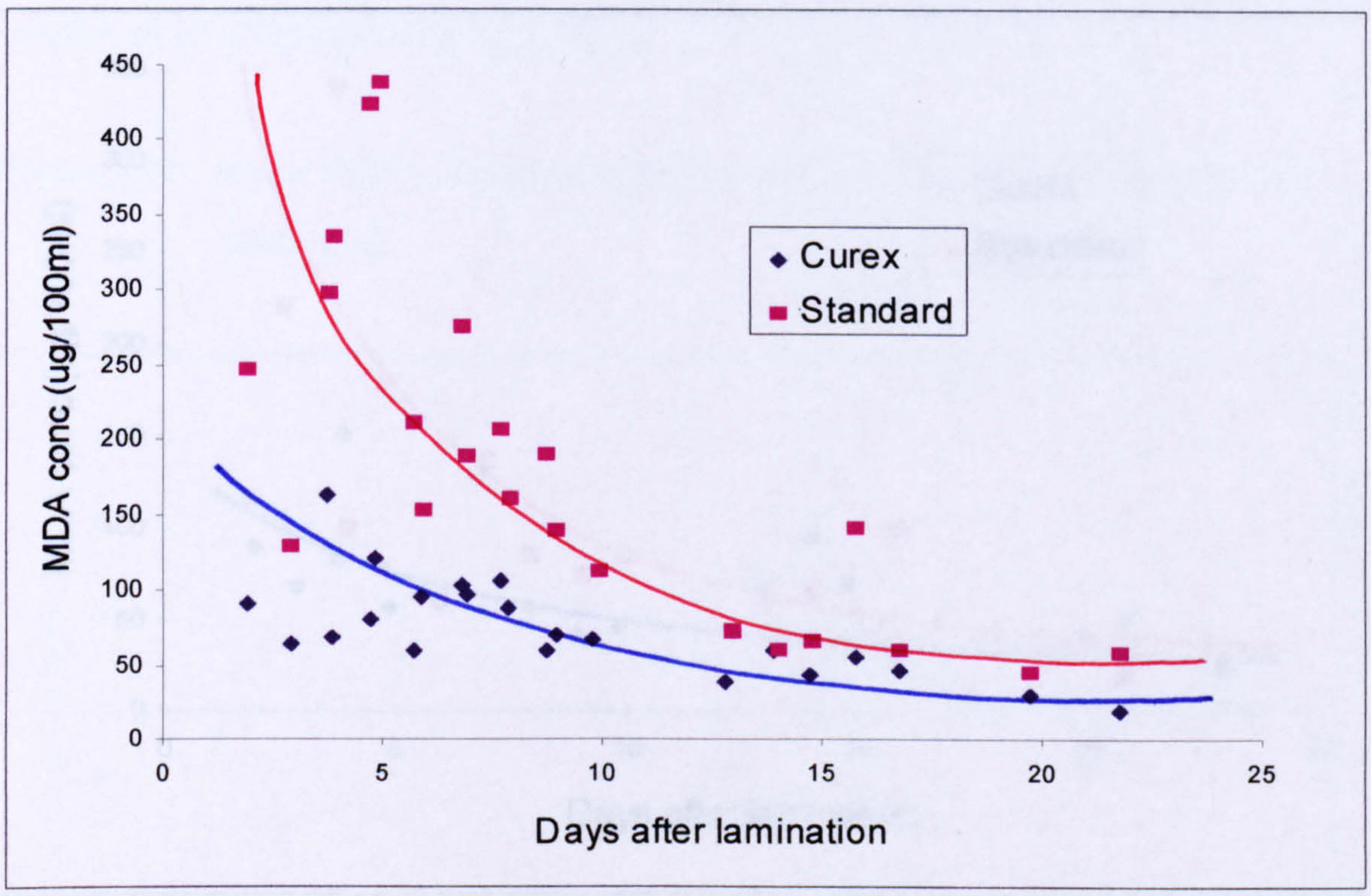
The initial level of migrating amine was very high in the case of sample 4, the one lacking any Curex. However this does reach a constant level after 15 days. In the case of the Curex sample 5, there is no rapid decrease in migrating amine levels detected just a steady almost linear slope to levels comparable with those observed in sample 4. Therefore it may be assumed that the initial amine level of sample 5 was comparable with that of sample 4 so this rapid decrease in free amine must of occurred in the two days before the sample was received and the first laminate pouches prepared.

Figure 3.8: Decay of amine (MDA) migration of samples 4 and 5 chopped in water, over time.



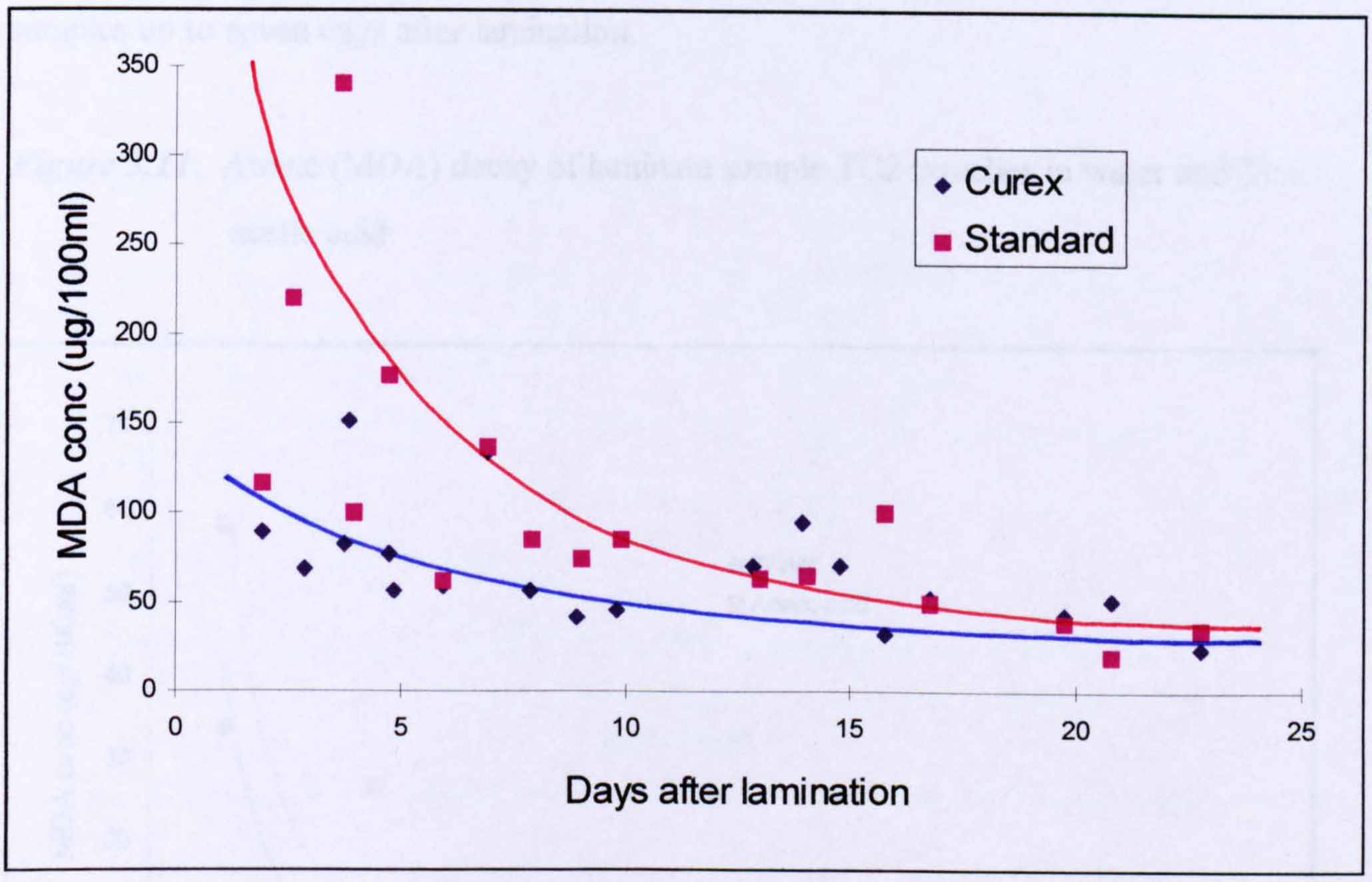
The differences in decay curves between the sample containing Curex and the one without are also reflected in the amine decay of chopped laminate samples into water. After approximately 15 days the levels are comparable which seems to suggest that the caprolactam only has an initial effect on the rate of amine decay and the curing process. The data points are very scattered probably due to uneven distribution of the solvent free adhesive during lamination resulting in varying intensities within the final laminate.

Figure 3.9: Decay of amine (MDA) migration of samples 4 and 5 pouches in 3% acetic acid, over time.



Again elevated migration levels are noted with the samples extracted into 3% acetic acid as the food simulant. The same decay patterns have also emerged between the sample containing curex and the one without, in both water and 3% acetic acid as both pouch and chopped samples. The scatter of the data may be due to variations within the laminate samples, work up of the laminate extracts or sensitivity of the method.

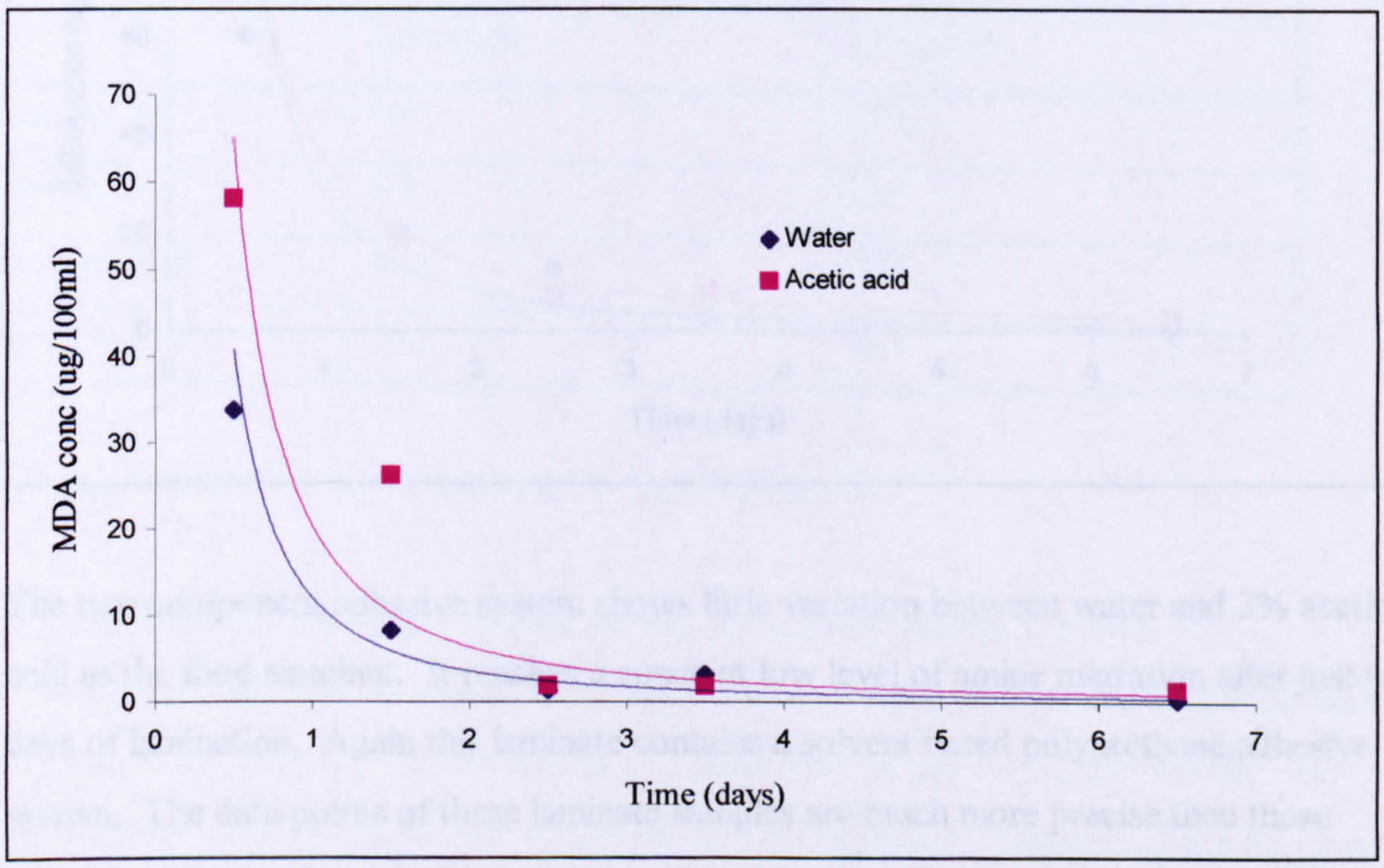
Figure 3.10: Decay of amine (MDA) migration of samples 4 and 5 chopped in 3% acetic acid, over time.



Again this shows a similar nature in the levels of amine migration, a rapid initial decay for sample 4 while a slow decay almost constant level of migratable amine is observed in sample 5 probably after a very rapid fall immediately after lamination prior to the sample being received by DMU. It appears that 3% acetic acid has a greater ability to facilitate migration in all laminate samples.

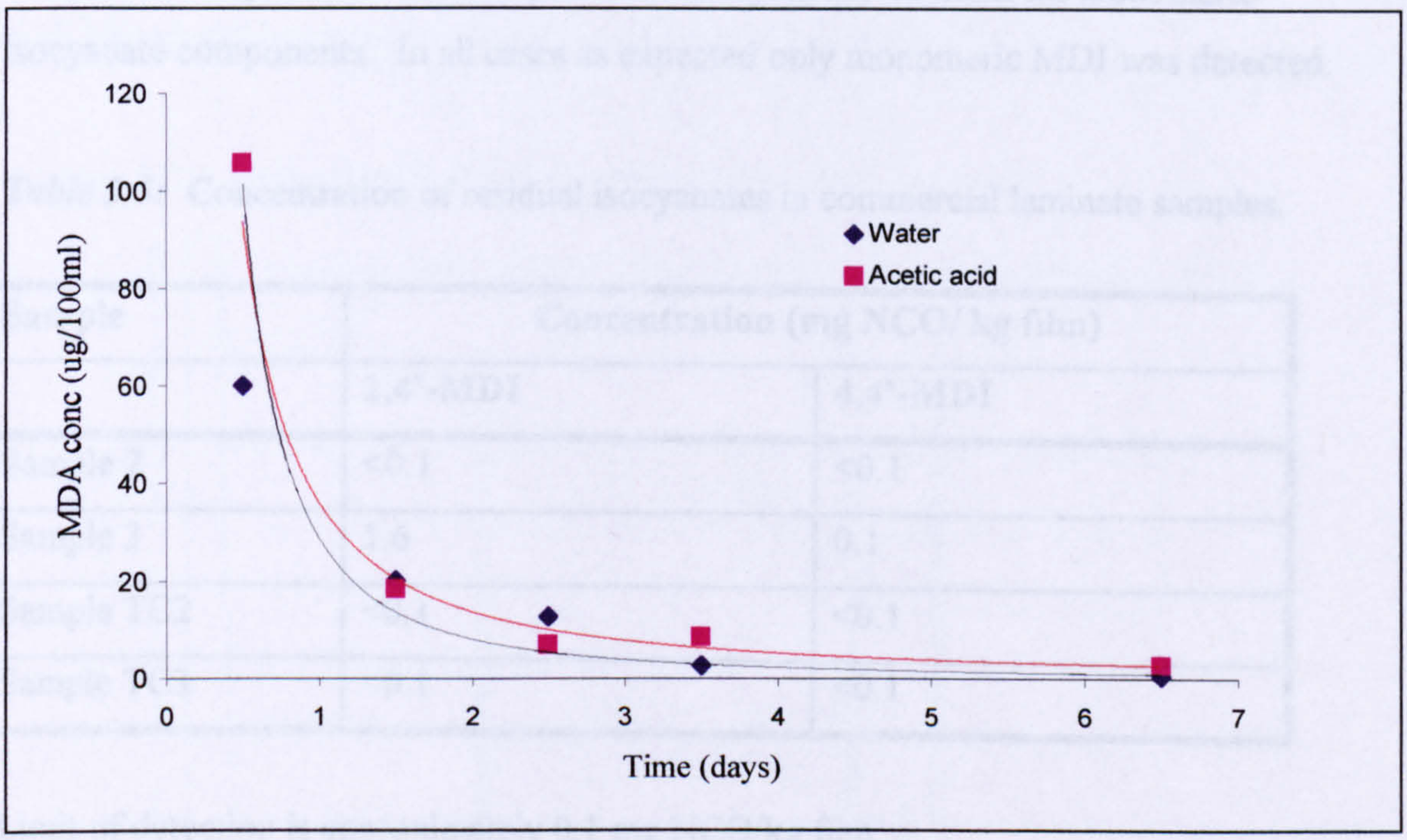
Two laminate samples both composed of the same plastic films were collected on the day of lamination. One containing a one component polyurethane system and the other a two component adhesive system. Migratable amine levels were determined from pouch samples up to seven days after lamination.

Figure 3.11: Amine (MDA) decay of laminate sample TC2 pouches in water and 3% acetic acid



This one component system shows acceptably low amine levels after just one day of the lamination process. This may be explained by the fact that this is a solvent based system and so the isocyanate content would be present at a lower excess than in a solvent free system.

Figure 3.12: Amine (MDA) decay of laminate sample TC3 pouches in water and 3% acetic acid



The two component adhesive system shows little variation between water and 3% acetic acid as the food simulant. It reaches a constant low level of amine migration after just two days of lamination. Again this laminate contains a solvent based polyurethane adhesive system. The data points of these laminate samples are much more precise than those noted for samples 4 and 5, this may be explained by the different carrier phases. These samples (TC2 and TC3) are solvent based and so distribution of the adhesive during lamination is better controlled and thus more evenly spread, unlike solvent free systems.

3.3.2 Derivatisation of the isocyanate group and analysis by HPLC

CSL carried out the CEN based method on six samples, four laminates and two wet isocyanate components. The samples were analysed for 12 different monomeric isocyanate components. In all cases as expected only monomeric MDI was detected.

Table 3.5: Concentration of residual isocyanates in commercial laminate samples.

Sample	Concentration (mg NCO/ kg film)	
	2,4'-MDI	4,4'-MDI
Sample 2	<0.1	<0.1
Sample 3	1.6	0.1
Sample TC2	<0.1	<0.1
Sample TC3	<0.1	<0.1

Limit of detection is approximately 0.1 mg NCO/kg film

These results only show the presence of MDI in laminate sample 3, a total of 1.7 mg NCO/ kg film two weeks after lamination, exceeding the specific migration limit of 1 mg NCO/ kg in the finished article. A higher level of the 2,4 isomer was detected probably due to steric hinderence of this isomer and so greater reactivity of the 4,4 isomer.

Table 3.6: Concentration of free NCO monomer in commercial isocyanate components.

Sample	2,4'-MDI	4,4'-MDI	Total MDI
Isocyanate component sample 2	<2 %	<2 %	2 %
Isocyanate component sample 3	38 %	21 %	59 %

Limit of detection is approximately 2%

The isocyanate component of adhesive sample 2 has not been detected and it is probable that it is present as either a pre-polymer or polymeric MDI.

Figures 3.13 and 3.14 show the HPLC chromatogram of the derivatised laminate extract and diluted wet isocyanate component of sample 3 respectively.

Figure 3.13: Derivatised isocyanate extract of laminate sample 3.

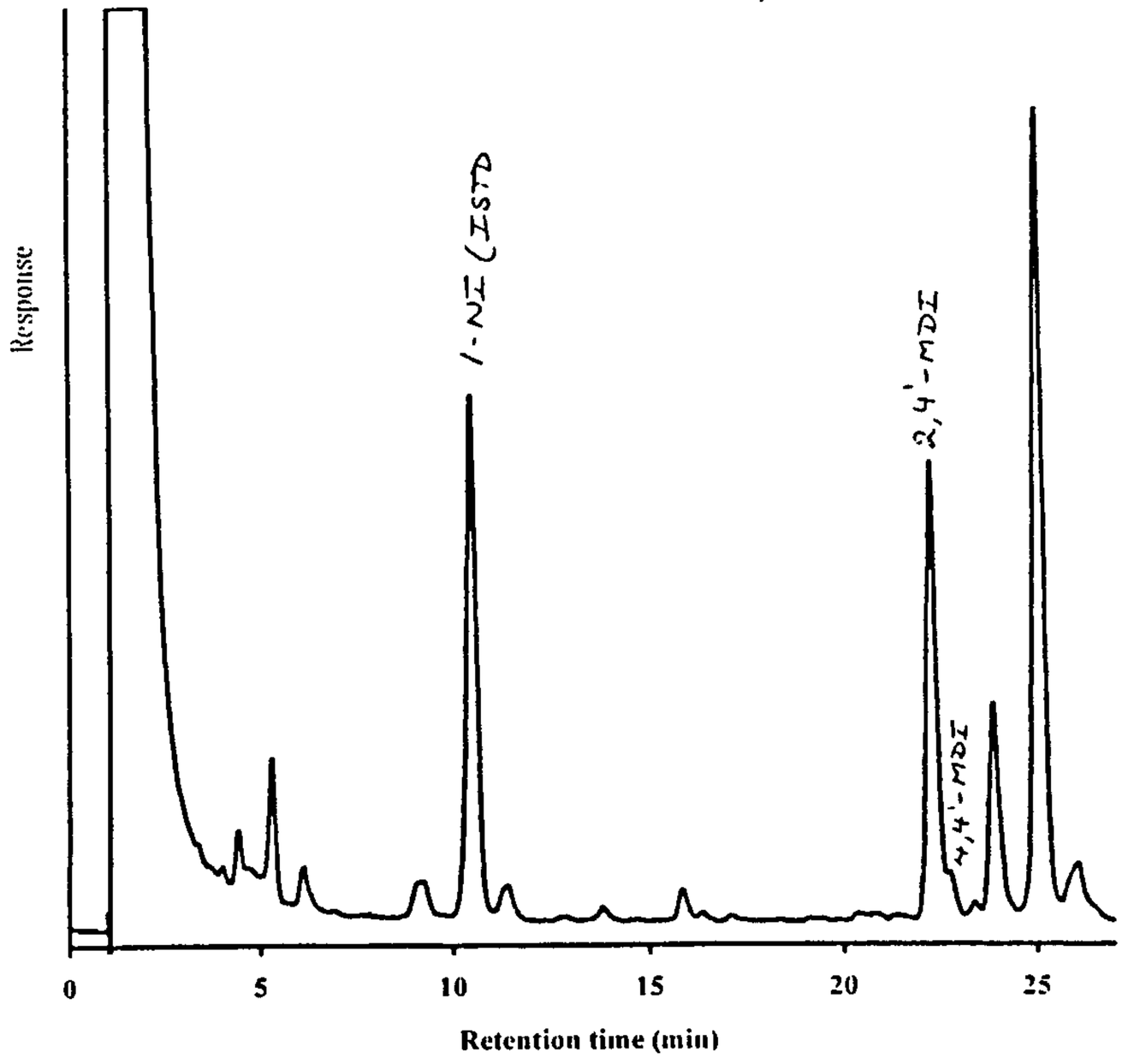
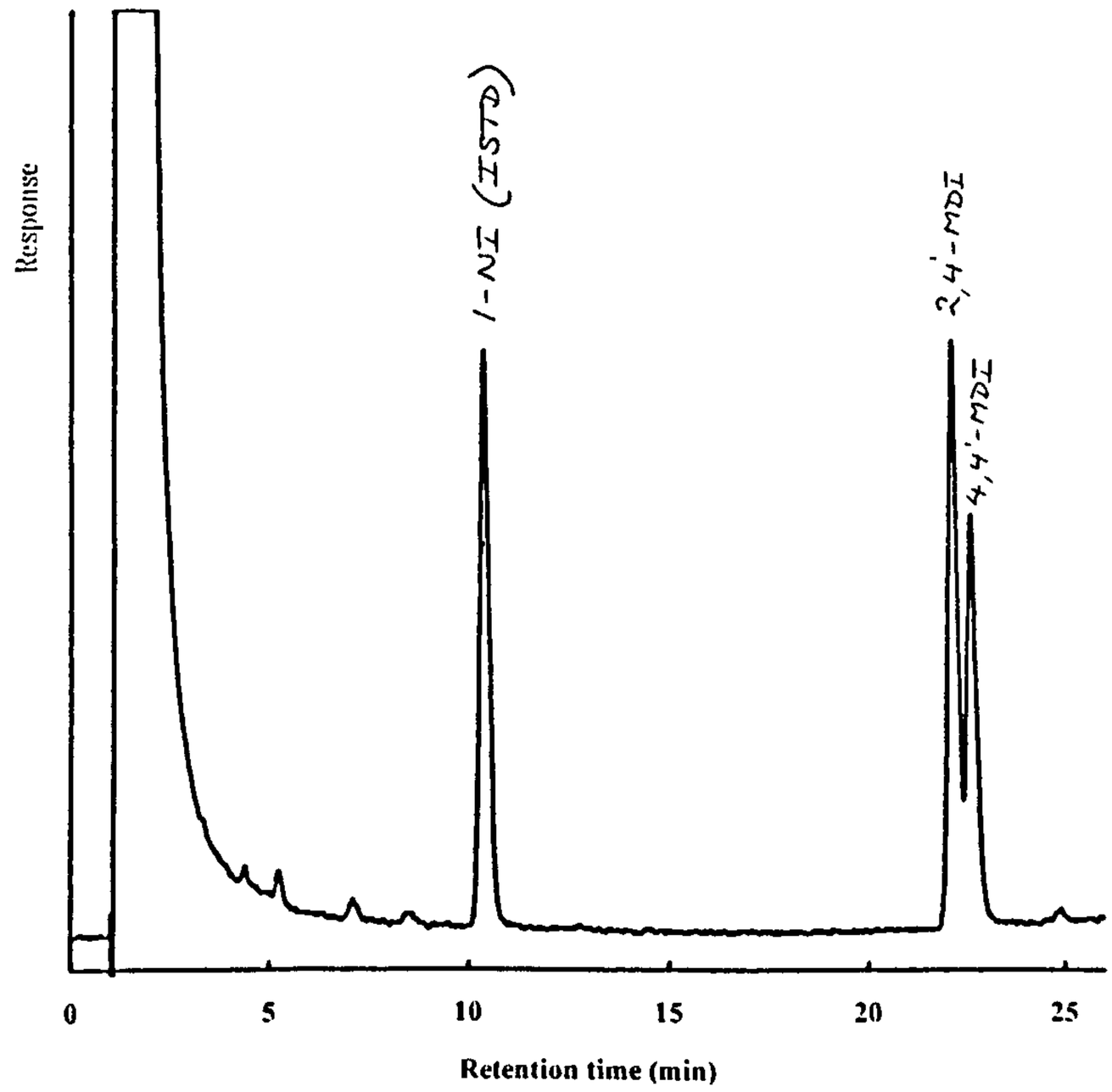


Figure 3.14: HPLC of derivatised isocyanate component sample 3.



3.3.3 Glycolysis of the isocyanate component

Five isocyanate components were cured and de-formulated using glycolysis with ethanolamine[49]. The observations of each cured sample were recorded prior to gylcolysis (Table 3.7).

Table 3.7: Observation of cured isocyanate component on aluminium foil prior to glycolysis.

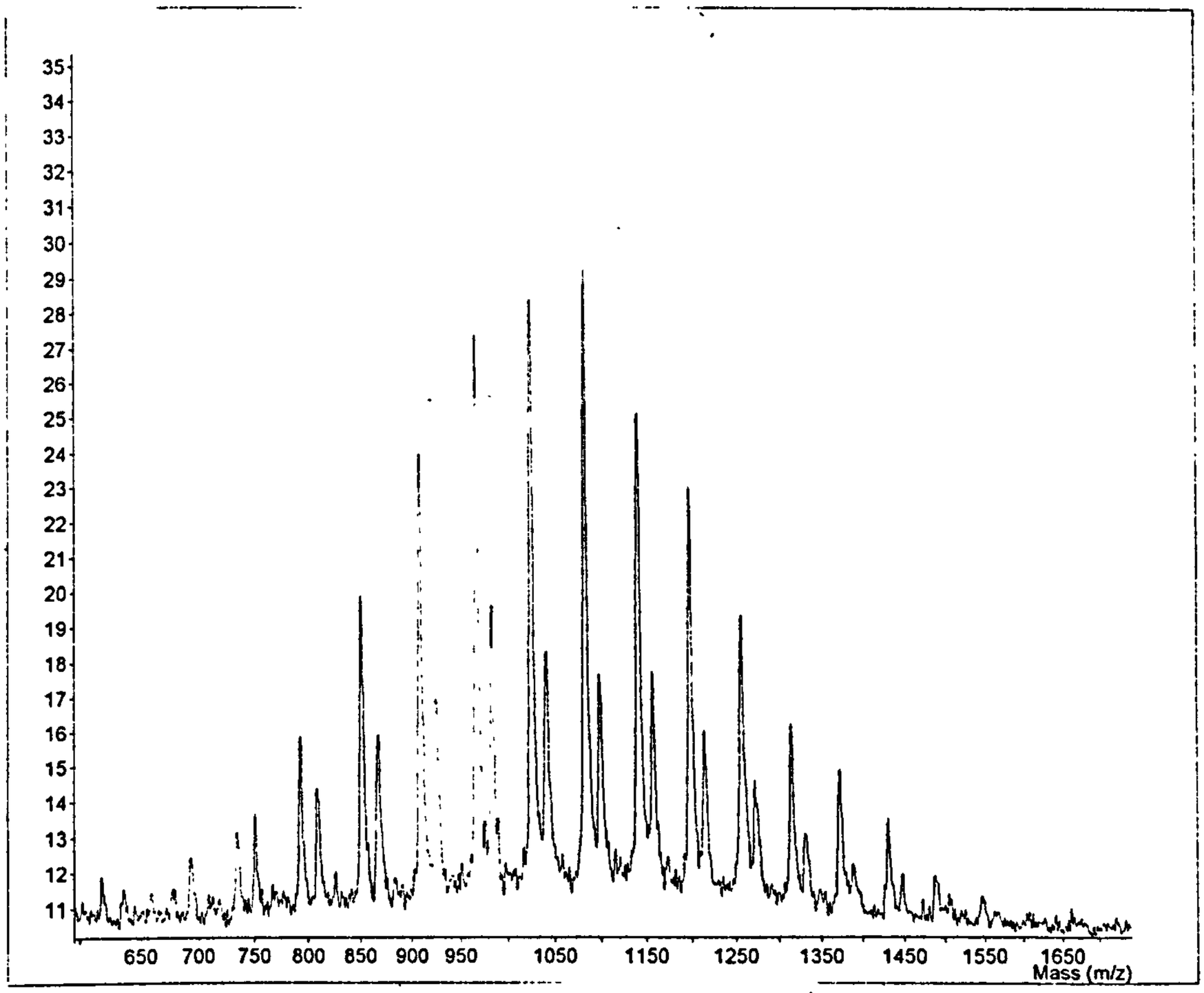
Sample	Observation
Sample 1	yellow - semi-rigid
Sample 2	white - flexible
Sample 3	orange - very brittle
Sample 4	white - flexible
Sample 5	white - flexible

It is inferred from these findings that the lighter the colour of the cured system, the more flexible it is. The cured component was then removed from the aluminium foil for glycolysis. After the glycolysis reaction, where polyol was present in the isocyanate component, the final mixture formed two layers, the top one of which contained the polyol. Hence where applicable a small amount of each layer was dissolved in acetonitrile for analysis by MALDI-MS.

Glycolysis of sample 1 resulted in the formation of a single layer which, when analysed by MALDI-MS, produced a single peak at 198 mass units corresponding to MDA, a reaction product of MDI with ethanolamine.

In sample 2 two layers formed after glycolysis indicating the presence of a polyol, the MALDI analysis of which produced a distribution of peaks around 1050 mass units (Figure 3.15)

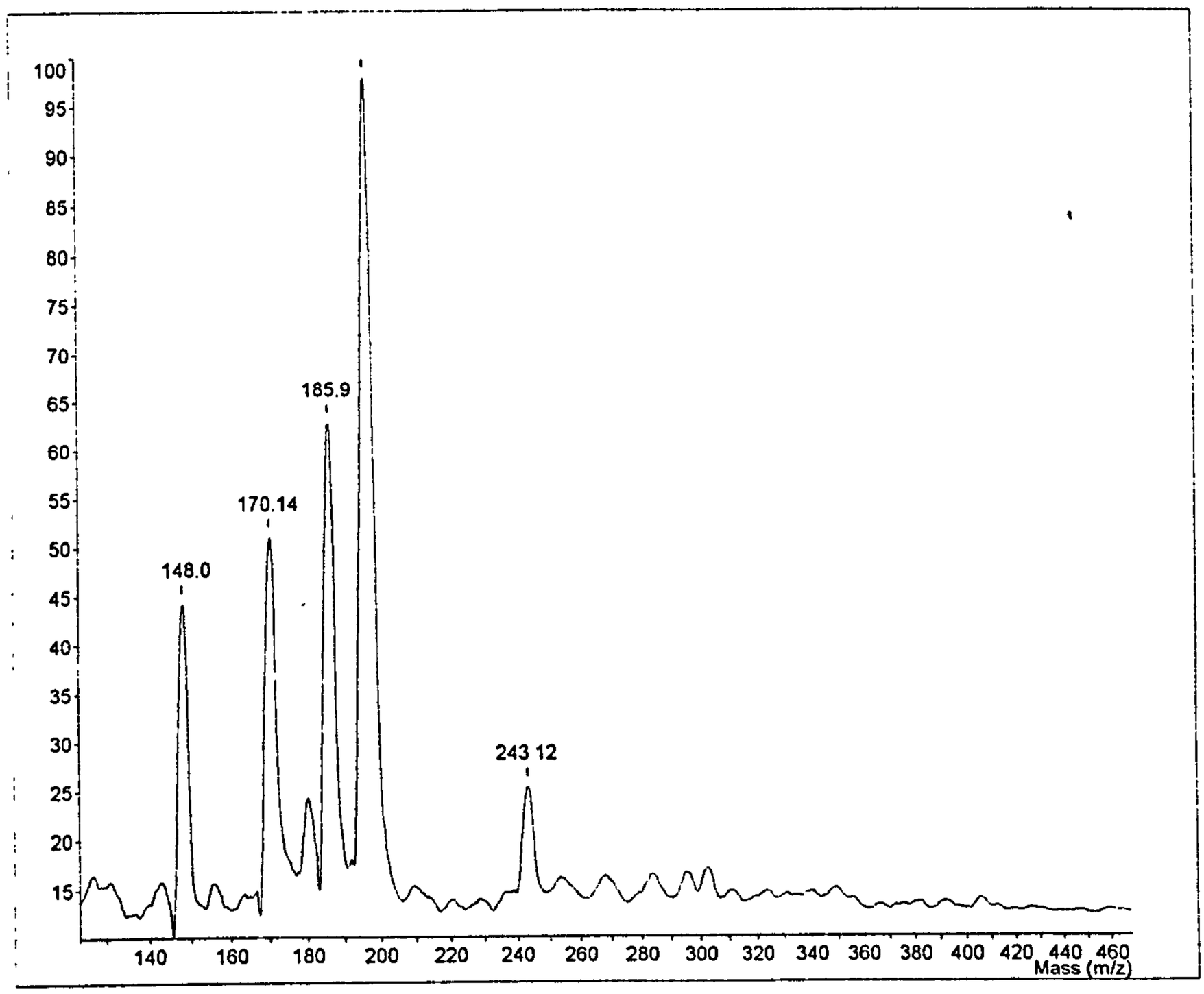
Figure 3.15: MALDI-MS of top layer of the glycolysis product of sample 2 in acetonitrile



This distribution of peaks corresponds to polypropylene glycol as the peaks are 58 mass units apart indicative of a propylene oxide repeat unit. The initiator used in the polymerisation of the polyether polyol can also be calculated from the mass spectral data. In this case propylene glycol appears to of been the starting initiator.

The glycolysis of sample 3 produced a single layer indicating the absence of any polyol in the isocyanate component. The MALDI of the single layer produced a peak for MDA (198) the reaction product of MDI and ethanolamine and three peaks corresponding to a reaction adduct of the glycolysis (Figure 3.16).

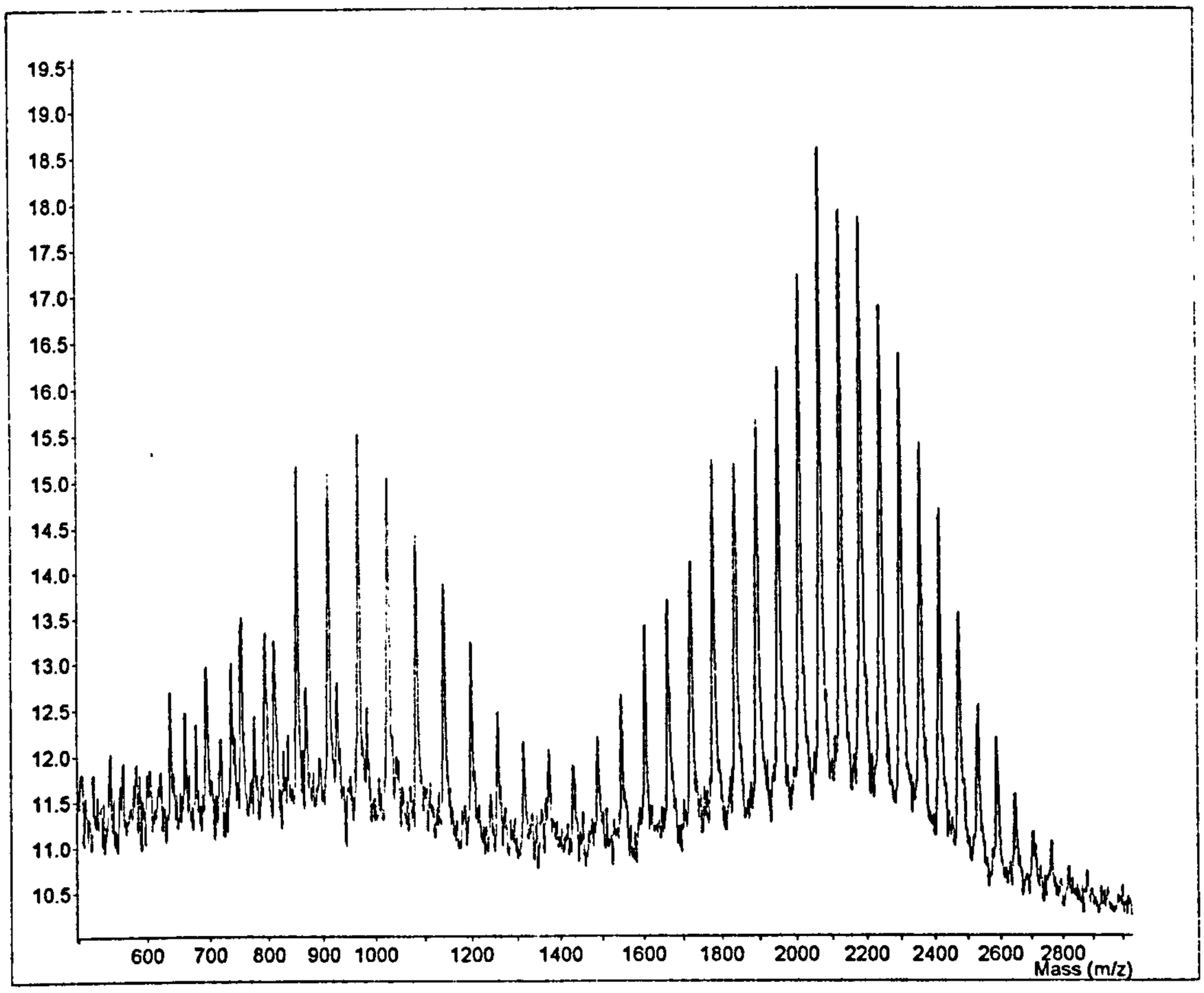
Figure 3.16: MALDI-MS of the single layer of the glycolysis product of sample 3 in acetonitrile.



The three peaks at 148.0, 170.14 and 185.9 are due to a reaction by-product 2-hydroxyethylcarbamic acid 2-aminoethylester (HECE) ($HOCH_2CH_2NHCOOCH_2CH_2NH$), the formation of this molecule is outlined in section 3.1, it appears as its molecular ion (148) and sodium and potassium cations.

The glycolysis of the isocyanate component of sample 4 produced a two layer product confirming the presence of a polyol. MALDI-MS was used to determine the nature of this polyol (Figure 3.17)

Figure 3.17: MALDI-MS of the top layer of sample 4 following glycolysis



The MALDI-MS of the lower layer produced the identical peaks to those observed in the single layer of sample 3 (figure 3.16). The upper layer produced two polyol distributions at 900 mass units and 2,000 mass units. The two peak distributions show the presence of two different polyols both based on propylene oxide repeat units and propylene glycol as the initiator for the distribution in the higher mass range and trimethylolpropane as the starter molecule for the distribution in the lower mass range. Hence the polyether in the lower mass range is trifunctional and that of the higher mass range is difunctional.

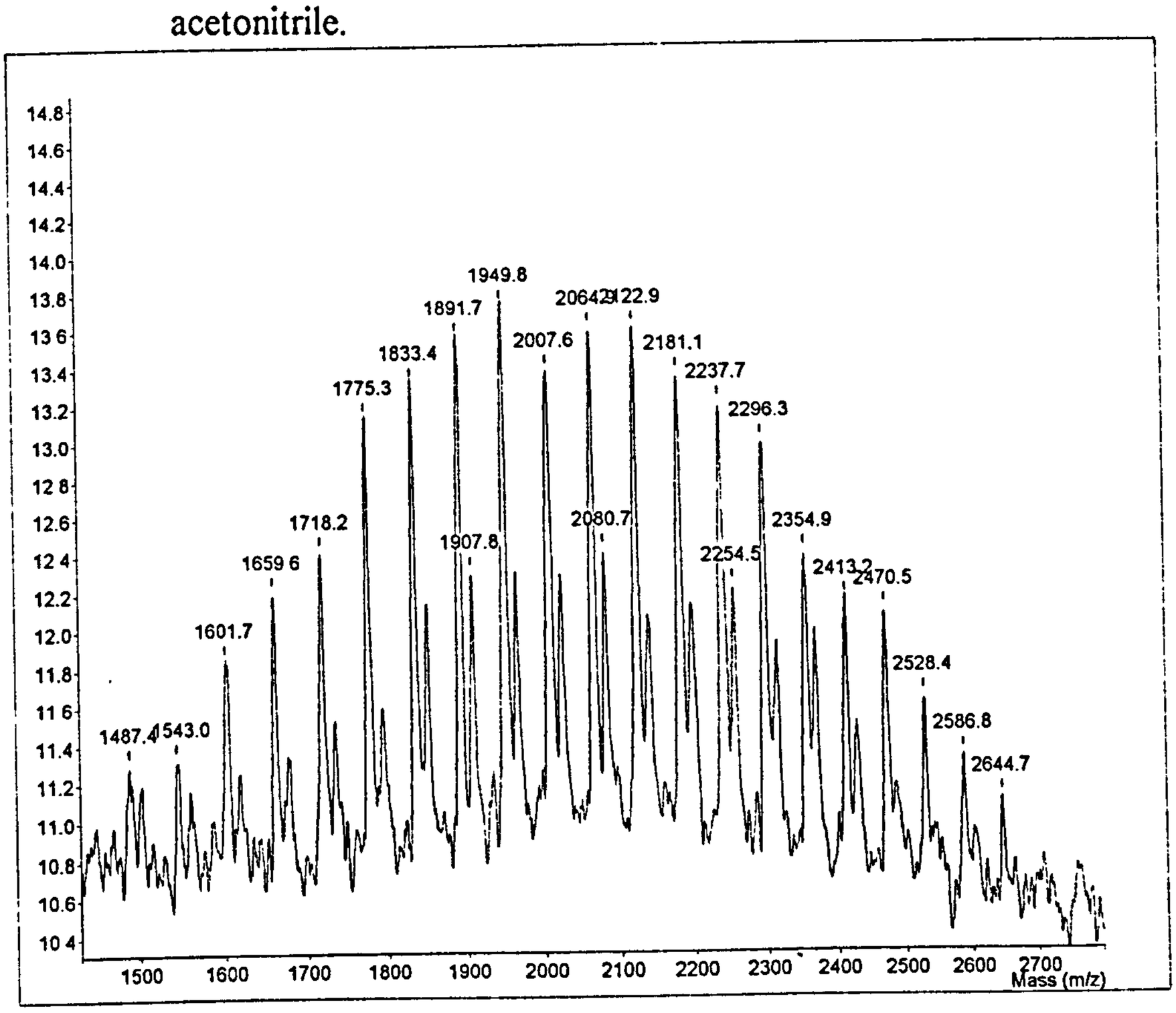
The presence of the two polyols indicates that the isocyanate component of this sample is either:-

a) A mixture of two prepolymers formulated with two different polyols.

or b) The reaction product from MDI plus a mixed polyol system

After glycolysis sample TC3 also formed two layers indicating the presence of a polyol. MALDI-MS of the lower layer detected MDA and the de-formulation adduct HECE, the same spectrum as that observed for sample 3 (Figure 3.16). The mass spectrum of the upper layer was used to calculate the nature of the polyol present in the original isocyanate component.

Figure 3.18: MALDI mass spectrum of the upper layer of sample TC3 after glycolysis in acetonitrile.



The mass units separating the peaks indicates that the polyol in the isocyanate component is a polypropylene glycol polyether polyol based on propylene glycol as the initiator. To give a difunctional polyether with an average molecular weight of 2,000.

3.4 DISCUSSION

Total amine determinations revealed that pouch samples TC2, TC3, sample 1 and 2 appeared to conform with the EU limit of total isocyanate levels based on the migration data determined. The manufacturer of sample 3 attributed its high levels to the cold conditions immediately after lamination and sent an identical sample (6) almost a week after lamination. This sample still produced high levels but they were approximately half that of sample 3. CSL also carried out HPLC analysis on sample 3 for monomeric isocyanate and their results confirm the high levels above the EU limit two weeks after lamination. Curex present in sample 5 did have an effect on the amine levels compared to sample 4 up to two weeks after lamination when both levels evened out. Curex is based on ε caprolactam and acts as an accelerator for polyurethane curing by reacting with the isocyanate to produce a tertiary amine which acts as a catalyst for the reaction between isocyanate and polyol. In all cases the amine levels in 3% acetic acid were higher. This suggests that the acetic acid is able to stabilise the amine (personal communication) and thus stop it reacting to form urea etc. In normal conditions amine levels are significantly lower than samples kept in dry conditions, probably due to the lack of moisture to initiate the formation of urea etc. in the dry samples.

The in-house Marcali method showed that in terms of mass to absorbance ratio the aniline hydrochloride is higher than MDA. This was unexpected due to the higher functionality of the latter, however the aniline hydrochloride has a higher extinction coefficient. Moreover the industrial method using solid phase extraction displayed quite the opposite order of calibration plots at a similar absorbance level to that of the in-house method. This could be due to the formation of amine terminated polyurea molecules coupled to the derivatising agent being retained on the SPE column due to their size. Hence if larger molecules are retained on the column it is questionable whether this method would be capable of detecting the derivatives of MDA. This is illustrated in the laminate sample

results, the industrial method gives approximately half the MDA amine levels and three quarters the aniline hydrochloride levels of that of the in-house method.

Total amine determinations based on the Marcali method will measure both monomeric and polymeric MDA present in solution. In all solvent free samples, polymeric MDI and hence polymeric MDA are present. The CSL HPLC based analysis does not measure polymeric derivatives as evidenced by their tests of a monomeric/polymeric isocyanate adhesive (sample 3) where only the monomeric species were detected. Similarly any polymeric MDA in the migrating species will not be detected. All of the detection methods (in-house, industrial and CSL) are subject to criticism. The amines measured by the Marcali method are assumed to be present in the polymer as NCO moieties which may not be the case (this may already be the amine). Only monomeric NCO moieties can be measured at CSL. Thus there is a need to confirm the nature of all species of possible concern within the laminate prior to measurement. None of the above methods has been shown to measure total residual NCO moieties only.

Glycolysis followed by MALDI mass spectroscopy appears to be an excellent method of determining the nature of the isocyanate component. In the commercial laminate samples used for these investigations, three out of the five wet components analysed were isocyanate prepolymers containing a long chain polyether polyol. These prepolymers will exhibit isocyanate functionality and so should be considered a potential hazard. However the CEN method is unable to detect them as illustrated in the HPLC analysis of the wet component of sample 2, and it is questionable whether these long chain isocyanates can be recovered from a solid phase extraction cartridge prior to amine determination using the industrial colorimetric method.

CHAPTER 4

ANALYSIS OF THE POLYOL COMPONENT

4.1 INTRODUCTION

The polyol component whether it be a polyether or polyester hydroxyl terminated compound is the initial macromolecule of most polyurethane systems and, as such, often forms the backbone of the final product, with the urethane bonds causing branching in the final polyurethane structure. Hence the final product's properties strongly depend on either the oligomer distribution or chemical composition of the polyol component. For instance, polyurethanes derived from linear polyols may be used as elastomers; lightly branched polyols give polyurethanes useful for flexible foams, while more heavily branched polyols are used in polyurethanes designed for application in rigid foams.

Polyethers are the most common polyols used in the production of polyurethane adhesives as they are inexpensive and offer high hydrolytic stability and good low temperature behaviour. Polyester based polyurethane adhesives are usually found in more demanding applications as they tend to be more expensive and more viscous which makes them harder to handle. However the resulting polyurethane offers good resistance to flexing, abrasion and many types of oil, they are less easily oxidised and resist higher temperatures than polyether based systems.

Little work has been published on the analysis of the polyol component in polyurethane systems, probably due to investigations of its more hazardous counterpart the isocyanate component (see chapter 3). There is no specific migration limit for the migration of the polyol component used in polyurethane adhesives for food contact use, although it is encapsulated in the overall migration limit of 10 mg/dm^2 or 60 mg/kg in the finished article stipulated in article 2 of the European Commission Directive 90/128/EEC.

Polyols are used in a number of other applications apart from polyurethane systems. These include: surfactants and wetting agents in laundry and industrial cleaners, solubilizers in enhanced oil recovery, ingredients in the cosmetic and food industries, emulsifiers in pharmaceutical preparations and solubility enhancers in biochemical membrane technology. Hence although little work is published with reference to the analysis of polyols in polyurethanes a number of separation techniques have appeared for the analysis of polyols used in other applications[53-66].

Relatively few highly efficient separation procedures are available in the literature. Basically three different approaches can be applied, each with its merits and drawbacks:

MALDI-MS -	Excellent identification power. Quantification is very problematic.
Size Exclusion Chromatography (SEC) -	Easy mass distribution determination. Poor separation efficiency.
Interaction chromatography -	Good separation efficiency and selectivity. Peak Identity and quantification can be difficult.

In the case of polyether polyols the most common method of analysis is liquid chromatography using a number of different detection methods[53]. Both gradient[54] and isocratic[55] HPLC techniques are well documented. The lack of an inherent chromophore in native polyethers either results in the use a range of detectors or the derivatisation of the hydroxyl groups. For example Refractive Index (RI) detection is applicable to all components regardless of whether they contain a chromophore or not. However it shows decreased sensitivity compared with signal monitoring by UV and is unsuitable for gradient analysis due to large deterioration as a result of the gradually changing RI signal.

Another method independent of the availability of chromophores in the molecule is Evaporative light-scattering detection (ELSD). It is a mass detector which is sensitive towards non-volatile compounds and so can be used with a wide range of solvents as mobile phases and in gradient HPLC. However this type of detector is rarely used for the analysis of polyether polyols, probably due to its absence from most analytical laboratories. One of the major limitations of the techniques cited above is the limited detection capability. In migration studies detection capabilities within the range $\mu g/cm^3$ and below are required and these are only available using derivatisation techniques. A number of compounds with appropriate UV-absorbing moiety have been used for the derivatisation of polyether polyols over a wide UV range. Such compounds include the incorporation of a benzoyl moiety at 254 nm[56] and 270 nm[57], and a 3,5-dinitrobenzoyl (DNB) residue at 254 nm[58,59]. The corresponding urethane derivatives can be obtained by reaction with phenyl isocyanate[60] and 1-naphtyl isocyanate[61] and measured at 240 and 291 nm respectively.

Compared to polyether polyols little information on the analysis of polyester polyols has been published. The majority of investigations have been carried out on polyethylene terephthalate (PET) using liquid chromatography coupled to mass spectroscopy in a number of ways including thermospray[62], atmospheric pressure chemical ionisation[63], fast atom bombardment[64] and plasma spray[65]. Methods of liquid chromatography include gradient reversed phase HPLC[66] and a two dimensional normal phase liquid adsorption chromatographic method under critical conditions with size exclusion chromatography[67]. Cyclic polyesters have been observed using LC-MS with both plasma spray[65] and fast atom bombardment[64]. The latter method was developed by Lawson et al[64] for the analysis of polyester oligomers used in polyurethane adhesives for food contact materials.

In this current study initial investigations were carried on the liquid polyol component where possible. Both known and unknown polyol samples were investigated to enable a fundamental understanding of the compounds at reasonable levels before trace analysis was performed on the more complex laminate systems. Once the nature of each polyol component was established, the natural progression was to assess the ability of these oligomers to migrate through an inner layer of laminate, usually polyethylene, into the space occupied by the foodstuff in a real life scenario. After establishing the potential for the polyol to migrate, trace analysis of the commercial laminate samples was carried out to determine both the nature and the quantity of migrating species from the polyol component.

A combination of analytical methods were used, initially MALDI-MS was used to gain an overall picture of the polyols and the migrants, with subsequent phenyl isocyanate derivatisation followed by HPLC analysis to quantify the migrating polyol species from the commercial laminate samples.

4.2 EXPERIMENTAL

4.2.1 Reagents

Millipore water (18MΩ)

HPLC grade acetonitrile and dichloroethane.

Glacial acetic acid and ethyl acetate

(Fisher Scientific, Loughborough, Leicestershire, UK)

Phenyl isocyanate, Gentisic acid

(Sigma-Aldrich, Gillingham, Dorset, UK)

Polypropylene glycol 1025

(BDH Limited, Poole, Dorset, UK)

Voranol P400, P1010, P2000

(Holden Surface Coatings Ltd, Bordesley Green, Birmingham, UK)

4.2.2 Apparatus

Pye Unicam PU4015 HPLC pump, Marathon autosampler,

Unicam UV-2-100 UV/VIS spectrometer

(Unicam, Cambridge, Cambridgeshire, UK)

Severn Analytical SA6500 detector, Spectra-physics datajet integrator

(Altech, Cornforth, Lancashire, UK)

Hulme Martin heat sealer - dual electronic

(Hulme-Martin Ltd, London, UK)

Finnigan Lasermat 2000

(Thermabio Analysis, Ashford, Middlesex, UK)

4.2.3 Samples

Liquid polyol samples of known composition were initially investigated, followed by the unknown liquid polyol samples provided with the commercial laminate samples. The composition of all of these materials are listed in Tables 4.1 and 4.2.

Table 4.1: Liquid polyols of known formulation and those provided with and used in the commercial laminate samples.

Liquid polyol sample	**Type**
Voranol P400	Polypropylene glycol (Mwt 400)
Voranol P1010	Polypropylene glycol (Mwt 1010)
Voranol P2000	Polypropylene glycol (Mwt 2000)
Sample TC1	Polyester (Adipic acid and diethylene glycol)
Sample TC2	Solvent based 1 component system based on polyether
Sample TC3	Solvent based 2 component system based on polyester
Sample 1	Solvent free polyether system
Sample 2	Solvent based polyether system
Sample 3	Solvent free polyester system
Sample 4 and 5	Solvent free polyester system

The following commercial laminate samples were made into pouches and analysed for any polyol migration through the inner layer of film which in every case is polyethylene.

Table 4.2: Commercial laminate samples analysed for polyol migration

Code	Configuration	Polyurethane	Coating weight
Sample TC1	45 μm PE / PU / 12 μm PET	Solvent free 2 component system	2.6 g/m^2
Sample TC2	45 μm PE / PU / 12 μm PET	Solvent based 1 component system	2.6 g/m^2
Sample TC3	45 μm PE / PU / 12 μm PET	Solvent based 2 component system	2.6 g/m^2
Sample 1	60 μm LDPE / PU / 12 μm PET	Solvent free 2 component system	2.4 g/m^2
Sample 2	75 μm LLDPE / PU / 12 μm MET PET (2g/m^2 PVDC)	Solent based 2 component system	2.5 g/m^2
Sample 3	45 μm (75:25 LDPE:BLLDPE) / PU / 12 μm PET	Solvent free 2 component system	1 - 1.5 g/m^2
Sample 4	50 μm LDPE / PU / 7 μm ALU / PET	Solvent free 2 component system	1.5 g/m^2
Sample JSD	70 μm LDPE / PU / 12 μm PET	unknown	unknown
Sample Z	70 μm LDPE / PU / 12 μm PET	unknown	unknown
Sample 481	70 μm LDPE / PU / 12 μm PET	unknown	unknown
Sample 484	70 μm LDPE / PU / 12 μm PET	unknown	unknown

4.2.4 Analysis of liquid polyol component

4.2.4.1 MALDI-MS analysis of liquid polyol in ethyl acetate

100 µl of the liquid polyol component was dissolved in 10 cm^3 ethyl acetate for analysis by MALDI-MS. 1 µl of this solution was then mixed with 1 µl matrix solution (0.1 g gentisic acid in 10 cm^3 water). After allowing the mixture to dry MALDI-MS was carried out on the samples. To check the validity of the MALDI-MS to detect the polyol oligomers generic samples of known mass distribution and functionality were also dissolved and analysed under the same conditions.

4.2.4.2 MALDI-MS of polyol extracted from cured adhesive system

Where possible the liquid isocyanate and polyol components were mixed in equal volumes and spread on aluminium foil. After allowing the polyurethane mixture to cure 1 g was removed from the foil and heated to 70°C for 2 hours in 10 cm^3 water. After removing the cured polyurethane from the water which was analysed by MALDI-MS as described in section 4.2.3.1.

4.2.4.3 Migration of liquid polyol through polyethylene film

1 g of liquid polyol was placed in a 5 cm^2 pouch made out of 45 µm polyethylene film heat sealed. The pouch was then placed in 100 cm^3 water and heated to 70°C for two hours, the pouch was removed from the water which was reduced to 5 cm^3 by rotary evaporation at 60°C. MALDI-MS analysis was performed on this residue in the same way as mentioned above (section 4.2.4.1). The resulting spectra were compared to those obtained from liquid analysis (section 4.2.4.1) to find the extent of possible migration. Where applicable the migrants from the pouch were quantified using a derivatisation method described in section 4.2.5.2.

4.2.5 Analysis of commercial laminate samples

4.2.5.1 MALDI-MS of commercial laminate extracts

Having established the nature of both the liquid polyol and the polyol extracted from the cured polyurethane and found potential to migrate, pouch samples of commercial laminates were analysed by MALDI-MS to determine the presence of any polyol. 20 cm^2 laminate pouches were prepared containing 100 cm^3 water and heated for 2 hours at 70°C, the water extract was then evaporated down to 10 cm^3 for analysis by MALDI-MS.

4.2.5.2 Quantification of polyether migrants

HPLC conditions - Column : Alphasil C18 5 µm 25 cm x 4.6 mm i.d
Mobile phase: acetonitrile : water (75:25), (70:30)
Flowrate: 2 ml/min
Wavelength: 240 nm

The lack of a chromophore in the polyether oligomers prevents conventional UV detection, unless the oligomers are derivatised. The mono-functional phenyl isocyanate was used to cap the hydroxyl functional groups in the polyethers and provide an aromatic ring for UV detection. Calibration curves were prepared using either the liquid polyol provided with the sample or generic materials of the same molar mass distribution and functionality. For all of the polyether based commercial laminates the MALDI-MS revealed the migration of two polypropylene glycol polyethers both with a mean molecular weight of 400, one being di-functional and the other tri-functional. Hence two calibrations were prepared using different mobile phases for better separation, (75:25) and (70:30) respectively. The derivatisation step was performed as follows:- 1 g of the liquid polyol

was dissolved in 10 cm^3 of dichloroethane, 200 µl of which was then heated for three hours on a heating mantle at 90°C with, 10.4 µl phenyl isocyanate in the case of the difunctional polyol and 14.8 µl phenyl isocyanate with the trifunctional polyol. The derivatised residue was then made up to 20 cm^3 in acetonitrile, 2,4,6 and 10 mg standards were then prepared in acetonitrile and run on the HPLC.´ The total peak areas of the derivatised polyether oligomers were plotted against the concentration of the standards. In the case of the laminate samples the pouch migrants where taken to dryness and dissolved in 200 µl dichloroethane and heated at 90°C for three hours with the relevant amount of phenyl isocyanate calculated from the overall migration results. (Chapter 2). For example, if the global migration was 1.0 mg then for the difunctional polyol:-

$$\frac{\text{mass}}{\text{rmm}} = \text{moles x polyol functionality} = \text{moles of phenyl isoscyante}$$

$$\text{moles x rmm (phenyl isocyante)} = \frac{\text{mass}}{\text{density}} = \text{volume}$$

so,

$$\frac{1.0\ \text{mg}}{420} = 0.00238 \text{ moles x } 2 = 0.00476 \text{ moles}$$

$$0.00476 \text{ moles x } 119.12 = \frac{0.567\ \text{mg}}{1.096} = 0.52\ \mu\text{l}$$

for the trifunctional polyol,

$$\frac{1.0\ \text{mg}}{440} = 0.0027 \text{ moles x } 3 = 0.00682 \text{ moles}$$

$$0.00682 \text{ moles x } 119.12 = \frac{0.812\ \text{mg}}{1.096} = 0.74\ \mu\text{l}$$

It is important to calculate the exact amount of phenyl isocyanate required to react with the polyol, as if it is added in too much excess then the isocyanate will react with itself to produce the urea and biuret etc. Hence it is necessary to know both the functionality and the mean molecular weight of the polyol before any derivatisations can be performed.

4.3 RESULTS

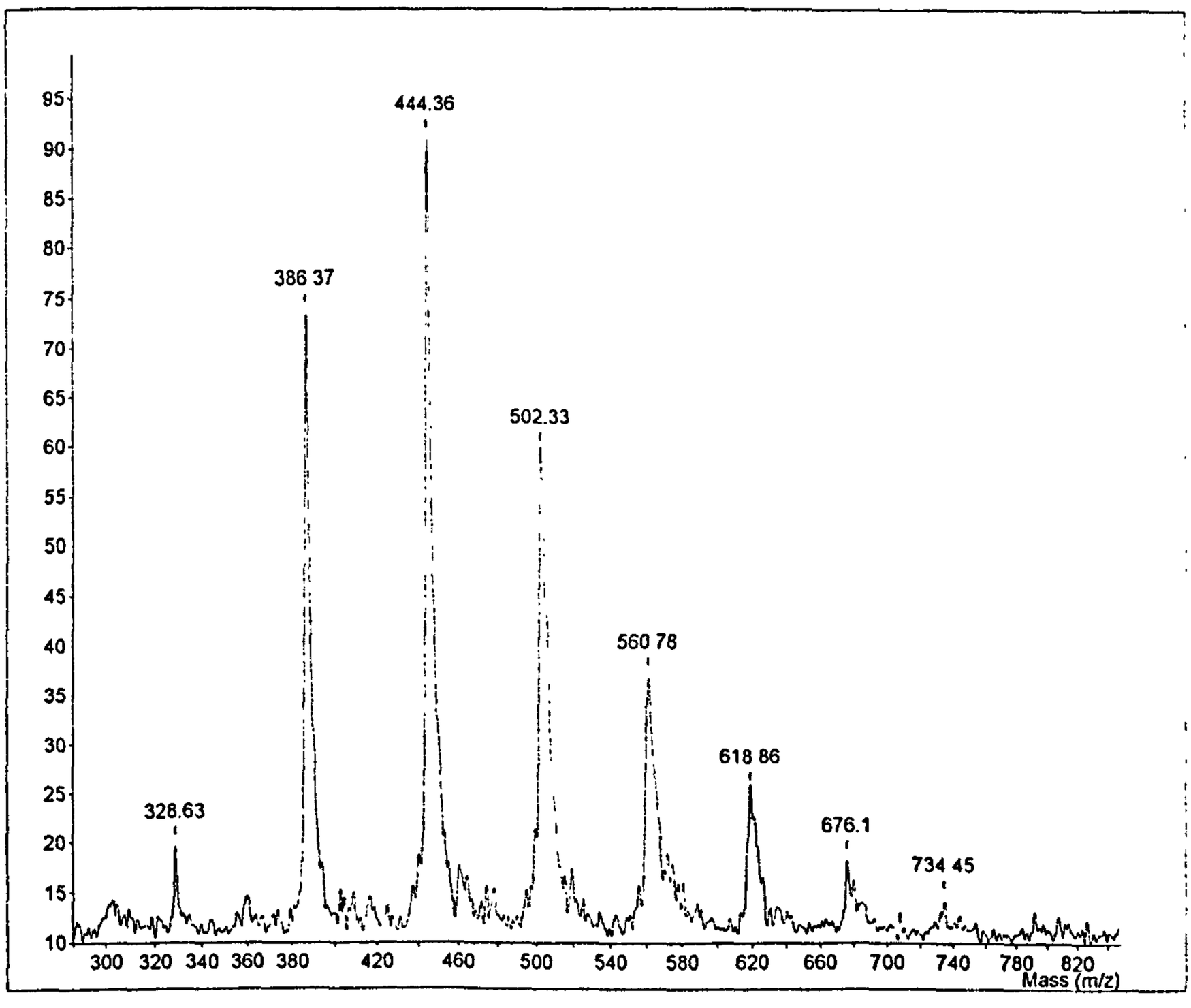
4.3.1 Analysis of liquid polyol component

Where the liquid components of the polyurethane adhesive were provided with the commercial materials analysis was carried out on the liquid to obtain an understanding of the polyurethane. Known samples were also analysed to confirm the ability of the analytical techniques applied.

4.3.1.1 MALDI-MS of liquid polyol in ethyl acetate

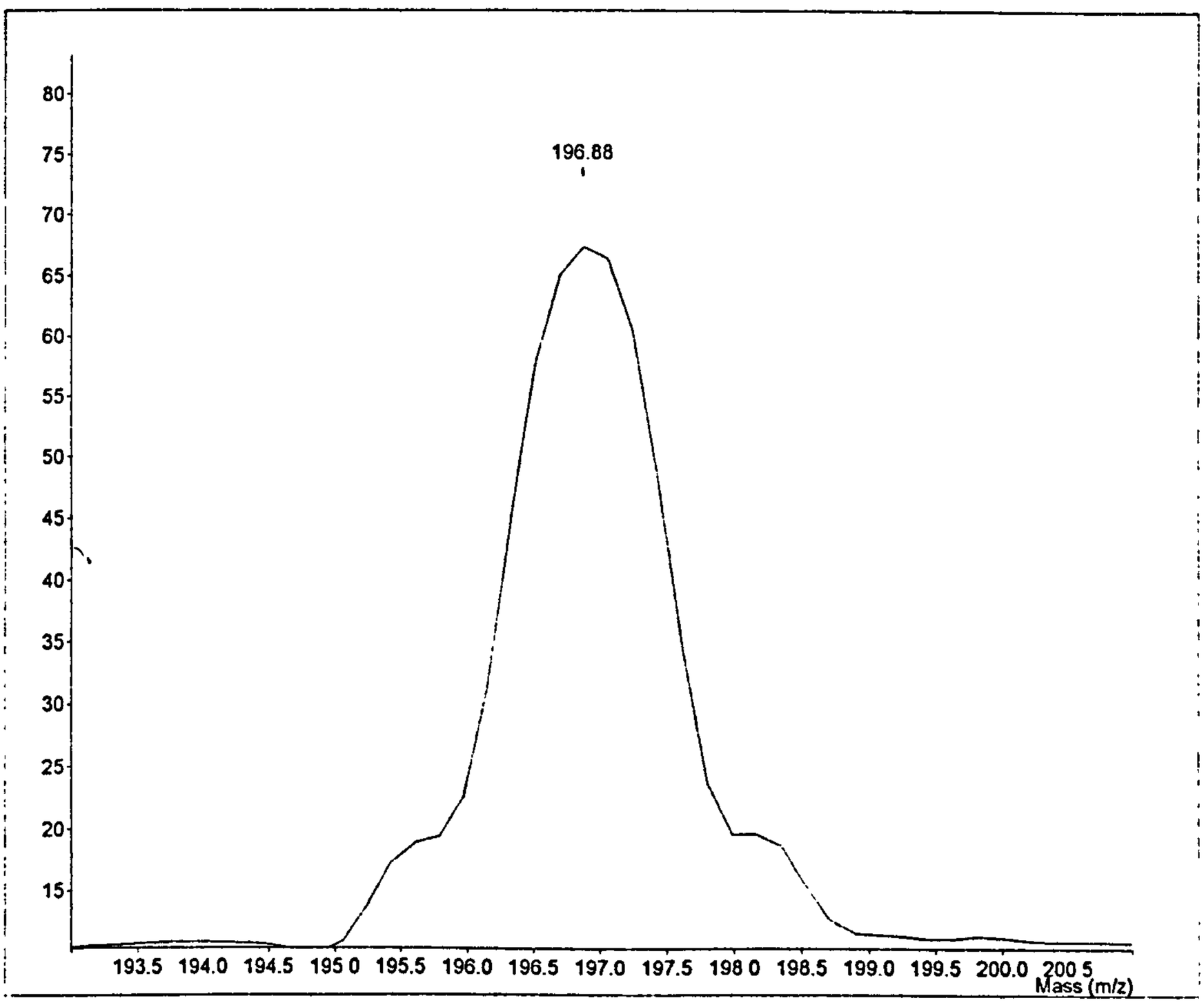
MALDI-MS analysis was carried out on all of the liquid polyols available. Known samples were investigated initially to check the ability of the MALDI and ensure all polyol oligomers could be detected. The Voranol samples are all difunctional propylene glycol molecules with varying mass distributions.

Figure 4.1: MALDI mass spectrum of liquid Voranol P400 in ethyl acetate



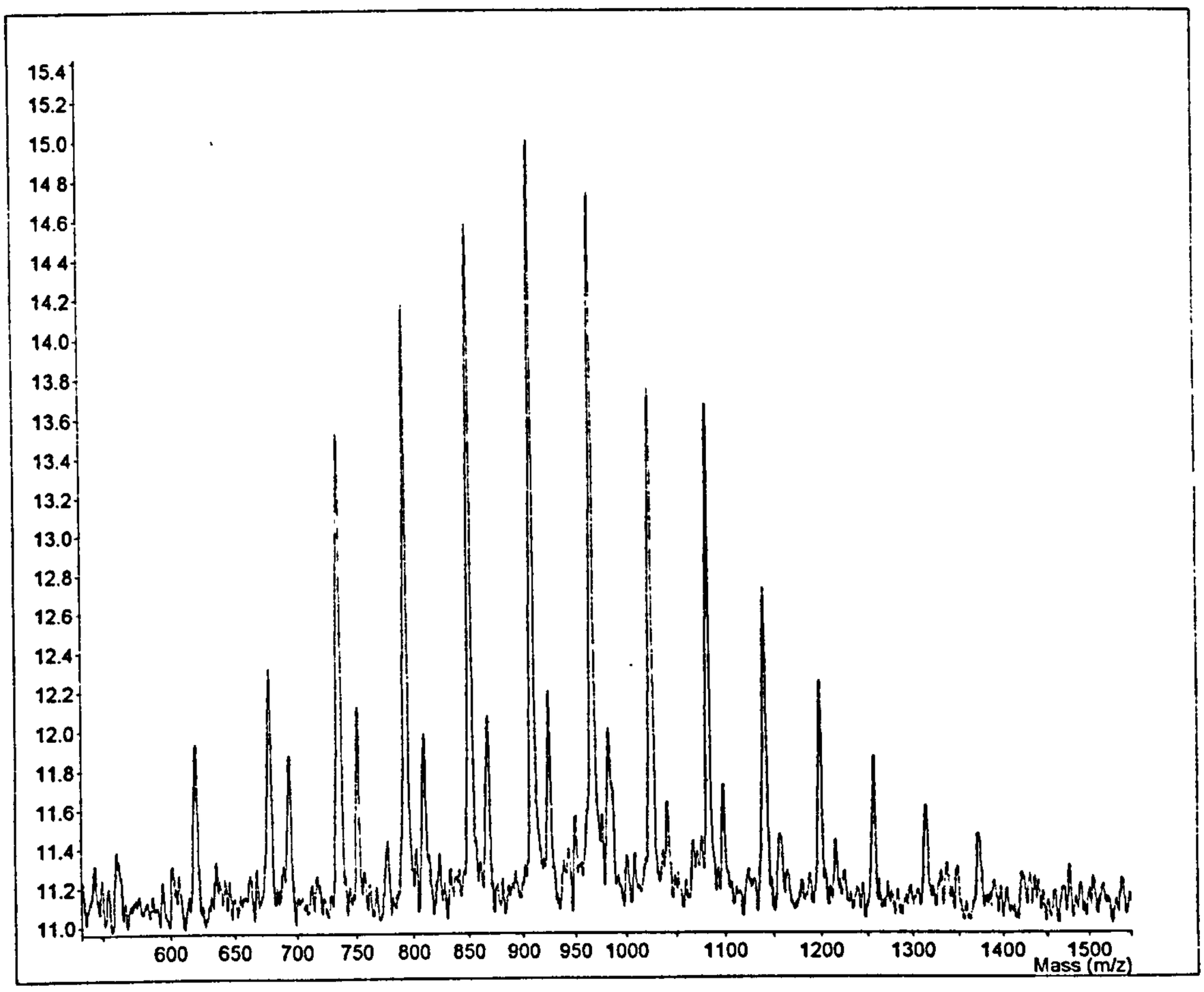
This spectrum shows eight oligomer peaks, each 58 mass units apart which corresponds to the repeat unit of the propylene oxide ($CH_2CH(CH_3)O$) molecule. Knowing the repeat unit it is then possible to calculate the initial starter molecule i.e. when n = 1. The mass of the initial molecule was calculated as 76 mass units which corresponds to propylene glycol. Hence the MALDI-MS confirmed that the Voranol P400 was a polypropylene glycol based on propylene glycol. However the MALDI data appears to be two mass units adrift in all cases which led to the analysis of a known sample of MDA which produces one peak.

Figure 4.2: MALDI mass spectrum of MDA in water



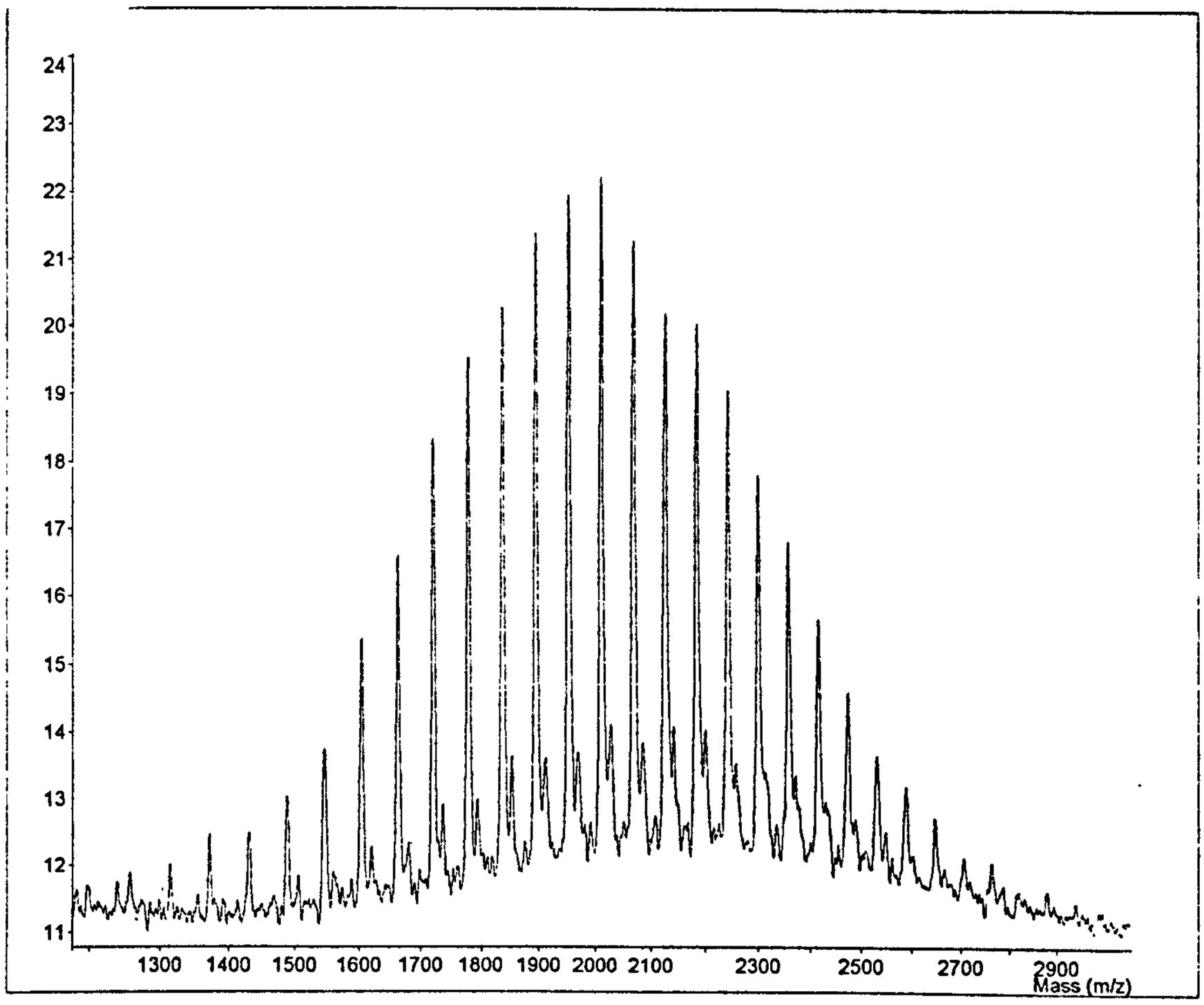
The exact mass of MDA is 198.27 whereas it is clear from the mass spectrum that the tip of the MDA peak is 196 - two mass units adrift. This confirms that the MALDI is two mass units out and so two units should by added to the peak values.

Figure 4.3: MALDI mass spectrum of liquid Voranol P1010 in ethyl acetate



This spectrum produced a nice distribution of peaks from 600 to 1,400 mass units, again each is 58 mass units apart indicating a propylene oxide repeat unit. The initial molecule was calculated to be propylene glycol, so again the MALDI-MS detected that Voranol P1010 was a difunctional polypropylene glycol polyether based on propylene glycol initiator.

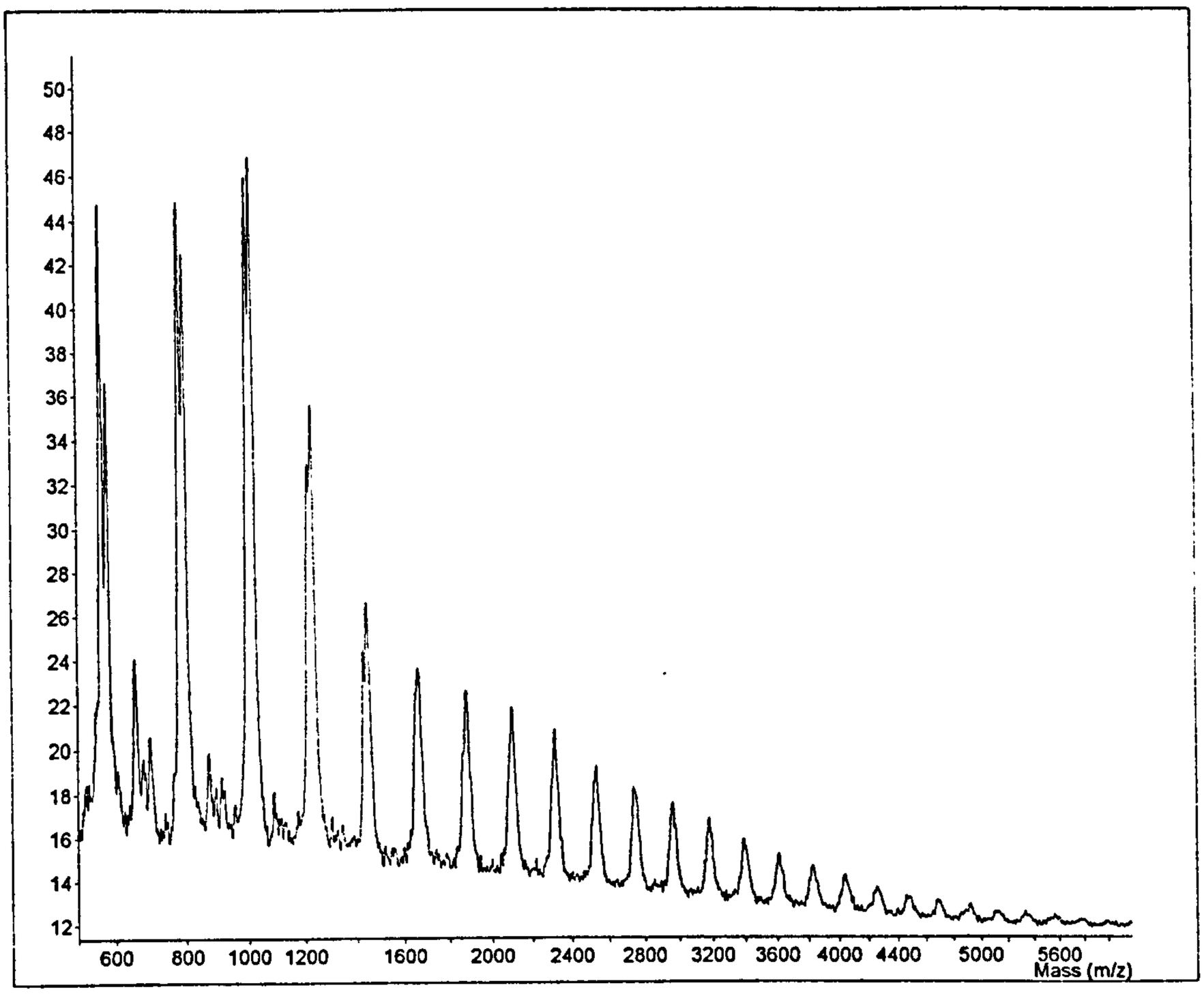
Figure 4.4: MALDI mass spectrum of liquid Voranol P2000 in ethyl acetate



This spectrum shows a large peak distribution from 1,300 to 2,700 mass units with a mean distribution around 2,000 mass units. In all, 26 oligomer peaks were detected, all 58 mass units apart confirming the presence of propylene oxide as the repeat unit. Calculations have also confirmed the initial molecule (n = 1) as propylene glycol corresponding with the chemical description.

The MALDI proved itself an excellent tool for the identification of polyether polyols. Next a known polyester polyol was run to assess the MALDI's ability to detect polyester oligomers.

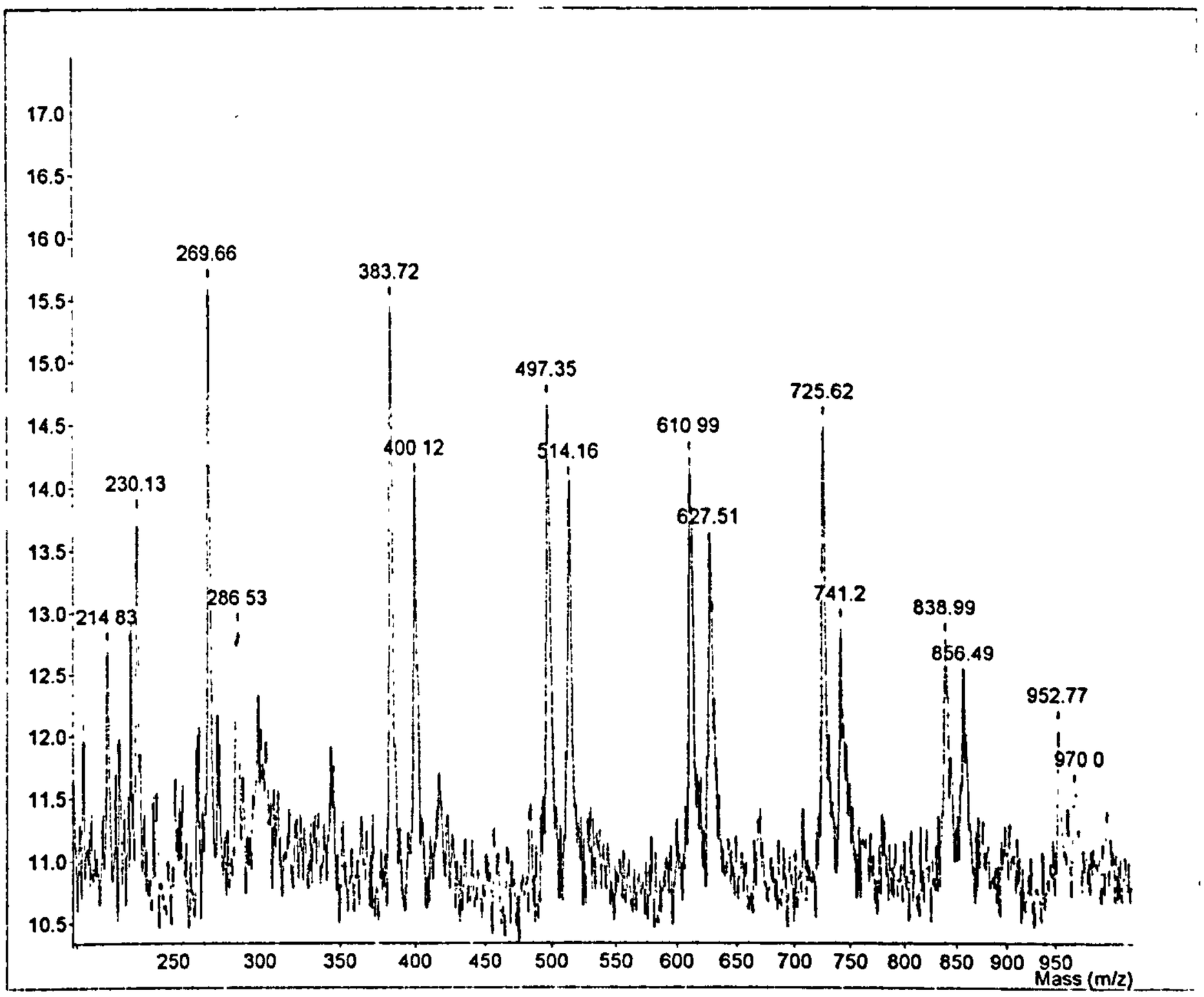
Figure 4.5: MALDI mass spectrum of liquid polyol sample TC1 in ethyl acetate



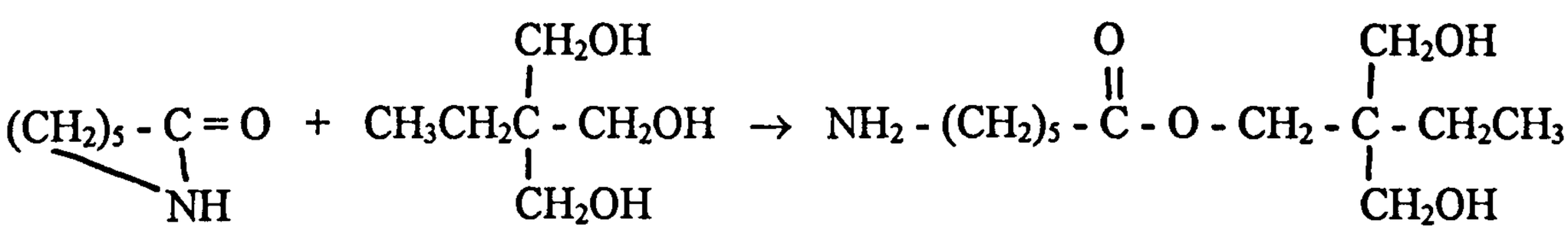
This polyester polyol is formulated with adipic acid (AA) and diethylene glycol (DEG). The MALDI mass spectrum shows a distribution of peaks from 500 to 5,500 mass units with decreasing peak abundance. The spectrum indicates the presence of 26 oligomers each separated by 216 mass units. Adipic acid has a molar mass of 146.14 and diethylene glycol is 106.12. A reaction of the two would produce a AA-DEG unit weighing 234.25 and a water molecule. In the formation of polyester polyols the glycol acts as a chain reaction initiator, and as polyesters for isocyanate work are always intended to be hydroxyl terminated, the glycol will be in excess in the original reaction mixture. Thus the adipic acid will almost always have a diethylene glycol unit on each end, so the first unit is DEG-AA-DEG with a mass of 322.34 and two water molecules, to which another -AA-DEG unit will attach giving a mass of 538.56 and four water molecules, a difference of 216 mass units. Hence each oligomer differs by the addition of an adipic acid and a diethylene glycol unit.

The ability of the MALDI-MS to detect both polyether and polyester polyol oligomers led to the analysis of the unknown liquid polyol components provided with some of the commercial laminate samples.

Figure 4.6: MALDI mass spectrum of liquid polyol sample TC3 in ethyl acetate



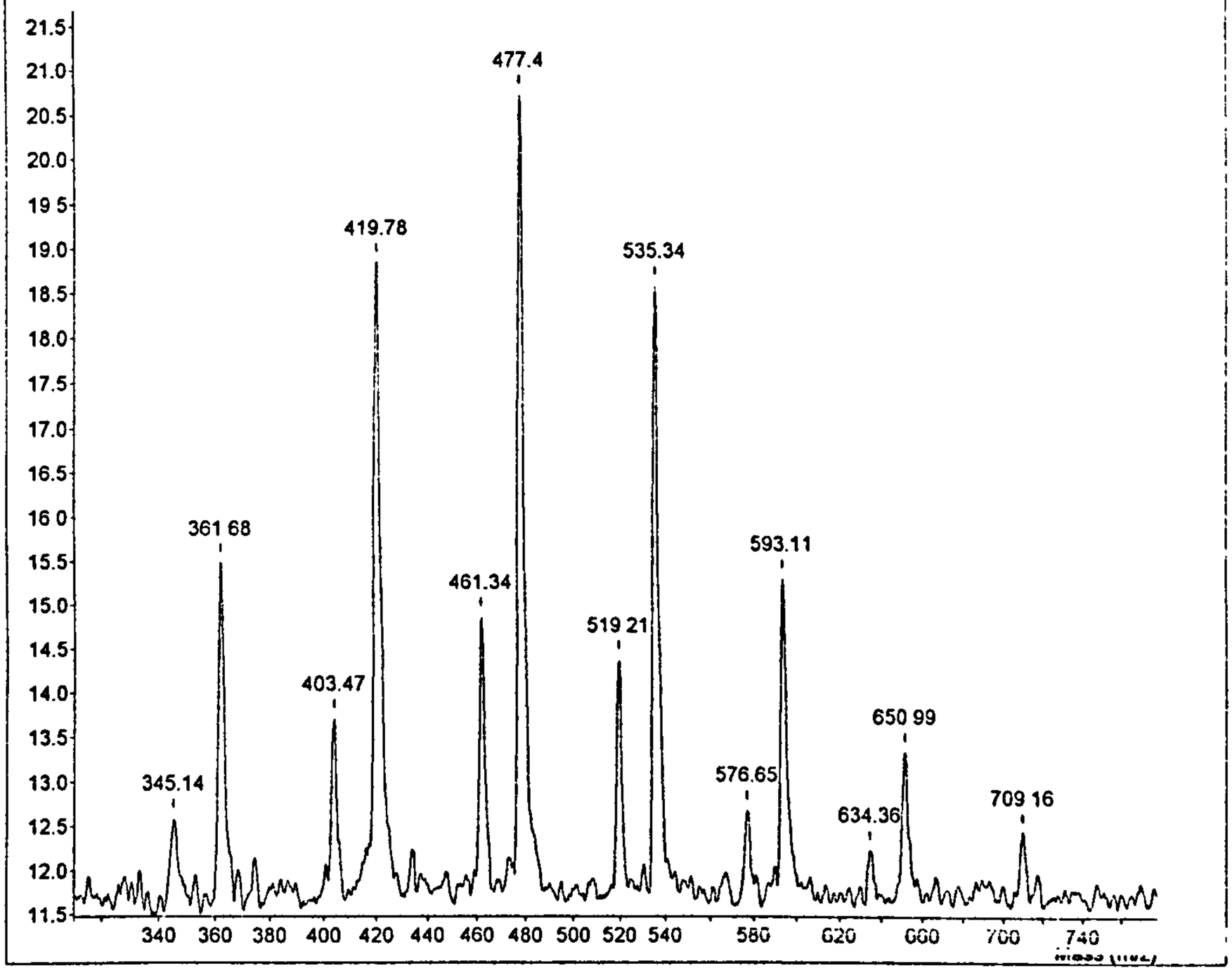
Seven pairs of peaks were detected by the MALDI-MS, each pair of peaks corresponding to the sodium and potassium cations of the same molecule. Each pair of peaks are 113 mass units apart indicating that caprolactam is the repeat molecule. To find the initial molecule the mass of caprolactam was subtracted from the mass unit of the first sodiated peak, this left a mass of 134 units corresponding to trimethylolpropane.



Caprolactam (CAP) Trimethylolpropane (TRI) CAP-TRI

Hence it has been deduced that the polyol component of sample TC3 is comprised of polycaprolactone with trimethylolpropane as the initiator.

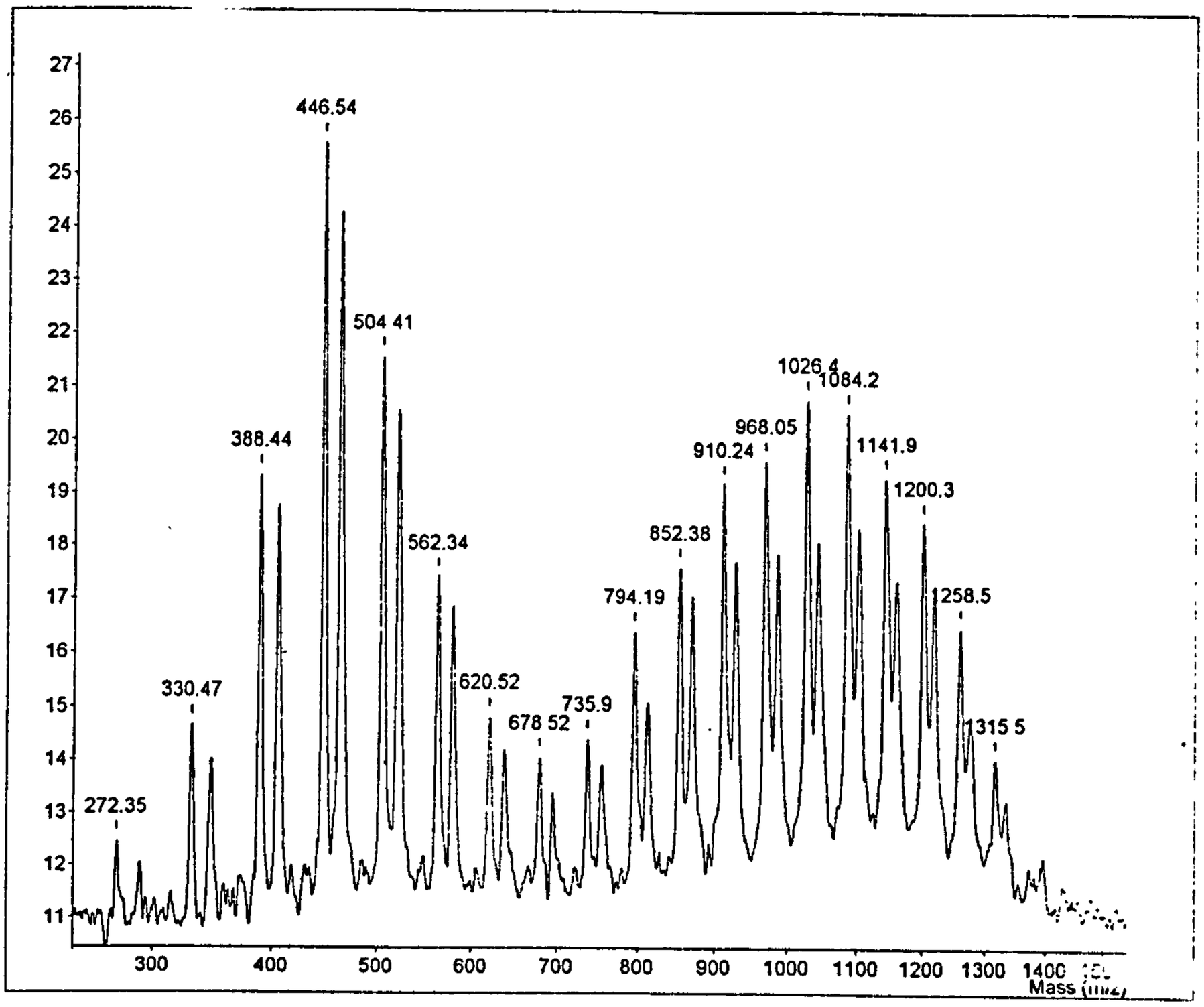
Figure 4.7: MALDI mass spectrum of liquid polyol component sample 1 in ethyl acetate



The MALDI-MS detected seven pairs of peaks, each pair again due to sodium and potassium cations of one oligomer. Each pair of peaks are 58 mass units apart indicating that propylene oxide is the repeat unit. Hence this is a polypropylene glycol polyether polyol. From this mass spectrum the initiator was deduced to be glycerol, hence this will be a trifunctional polyether.

$$\begin{array}{l} CH_2 - O\,(CH_2CH(CH_3)\,O)_n - H \\ | \\ CH - O\,(CH_2CH(CH_3)\,O)_n - H \\ | \\ CH_2 - O\,(CH_2CH(CH_3)\,O)_n - H \end{array}$$

Figure 4.8: MALDI mass spectrum of liquid polyol component sample 2 in ethyl acetate

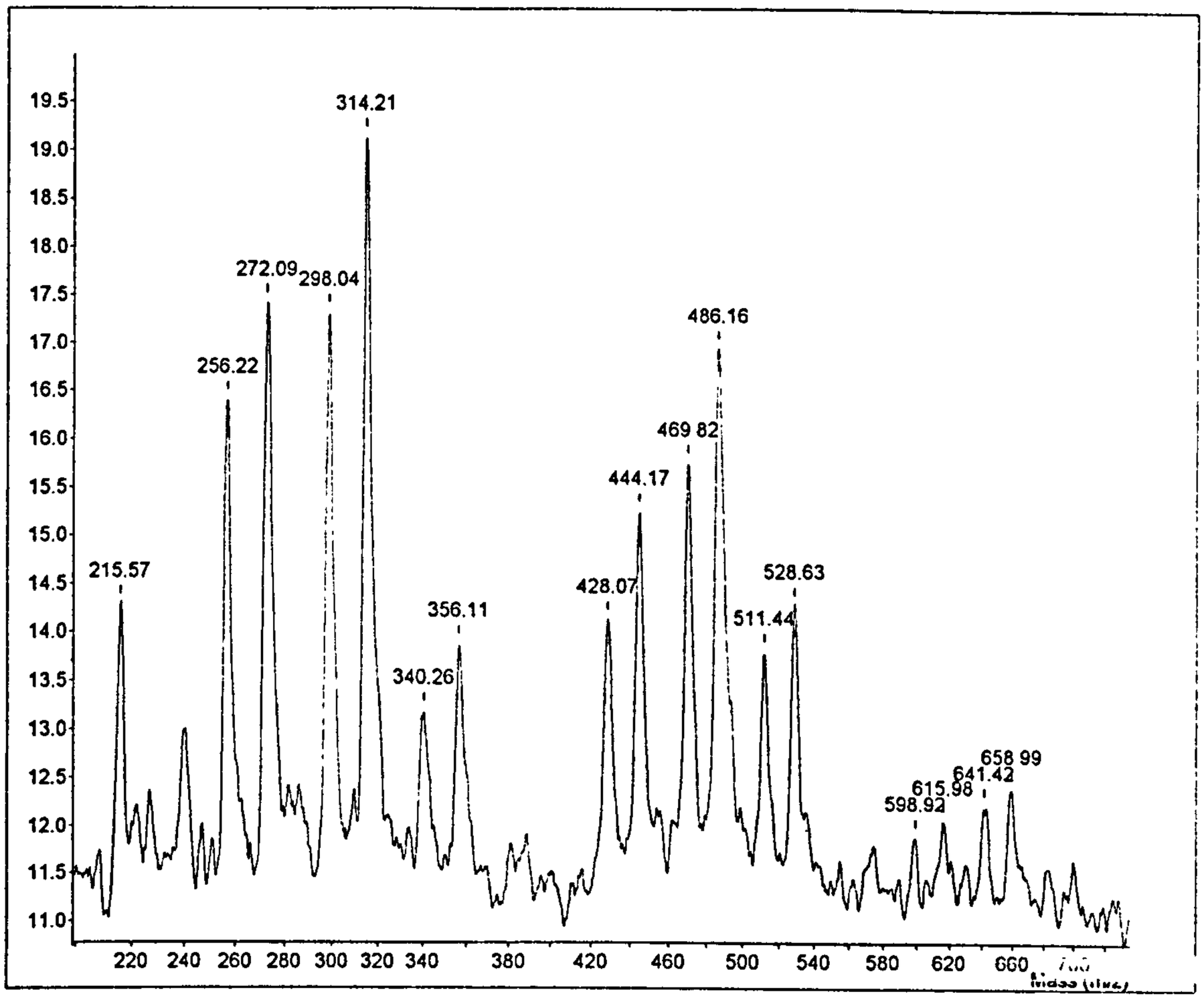


Again the spectrum shows pairs of peaks due to sodium and potassium derivatives of the same molecule. The peak distributions are detected by the MALDI, one with a mean molar mass of 420 and the other at 1,000. In all 19 oligomers are present all 58 mass units apart indicating that the polyol of both distributions is polypropylene glycol. Further calculations indicate that propylene glycol is the initiator, giving a difunctional polyol.

$$HOCH_2CH(CH_3)O\text{-}(CH_2CH(CH_3)O)_n\text{ - }H$$

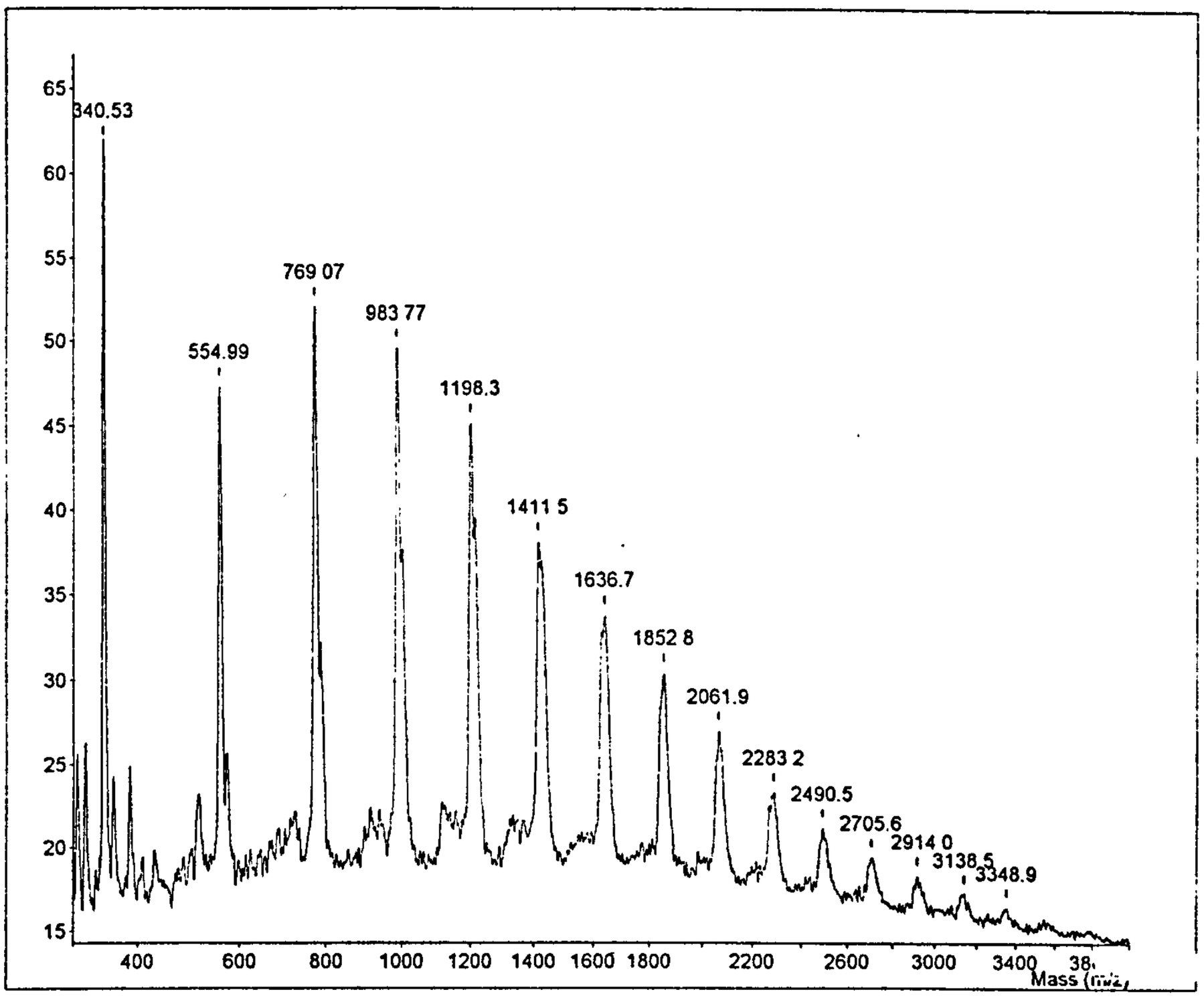
It appears that two polyols of the same composition but different chain lengths have been mixed.

Figure 4.9: MALDI mass spectrum of liquid polyol component sample 3 in ethyl acetate



The MALDI detected three sets of peaks, within each set the peaks are in pairs due to sodium and potassium cations. Hence each set of peaks contains three oligomers. From the peak patterns within each group and between groups, it was deduced that this is a polyester polyol composed a two glycols ethylene glycol (EG) and neopentyl glycol (NPG) and one carboxylic acid adipic acid (AA). The first set of peaks correspond to oligomers EG-AA-EG, EG-AA-NPG and NPG-AA-NPG respectively. The second set represent EG-$(AA\text{-}EG)_2$, NPG-$(AA\text{-}EG)_2$ and EG-$(AA\text{-}NPG)_2$. While the final set correspond to EG$(AA\text{-}EG)_3$ and NPG-$(AA\text{-}EG)_3$ respectively.

Figure 4.10: MALDI mass spectrum of liquid polyol component sample 4 and 5 in ethyl acetate



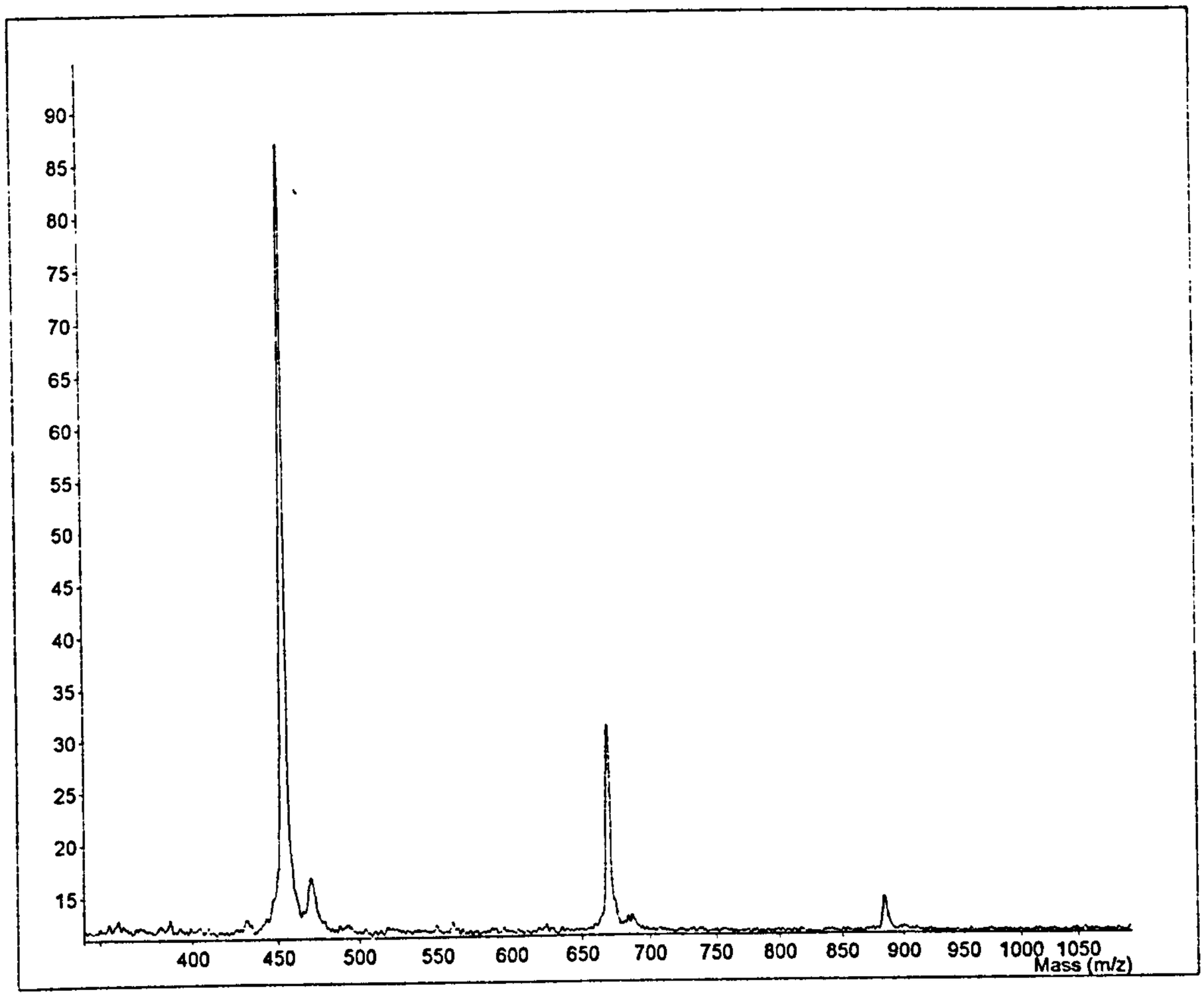
The MALDI mass spectrum shows a distribution of peaks from 550 to 3,350 mass units with decreasing abundance. The spectrum detected 14 oligomer peaks, each peak separated by 214 mass units. Combinations of the carboxylic acid and glycols were calculated to fit the mass gap. It was deduced that adipic acid (AA) and neopentyl glycol (NPG) were the starting compounds:

i.e. $NPG\text{-}(AA\text{-}NPG)_n$

4.3.1.2 MALDI-MS of polyol extracted from cured adhesive systems

The polyol and isocyanate wet components were mixed and cured on aluminium foil and extracted into water.

Figure 4.11: MALDI mass spectrum of urethane sample TC1 cured on aluminium foil and extracted into water



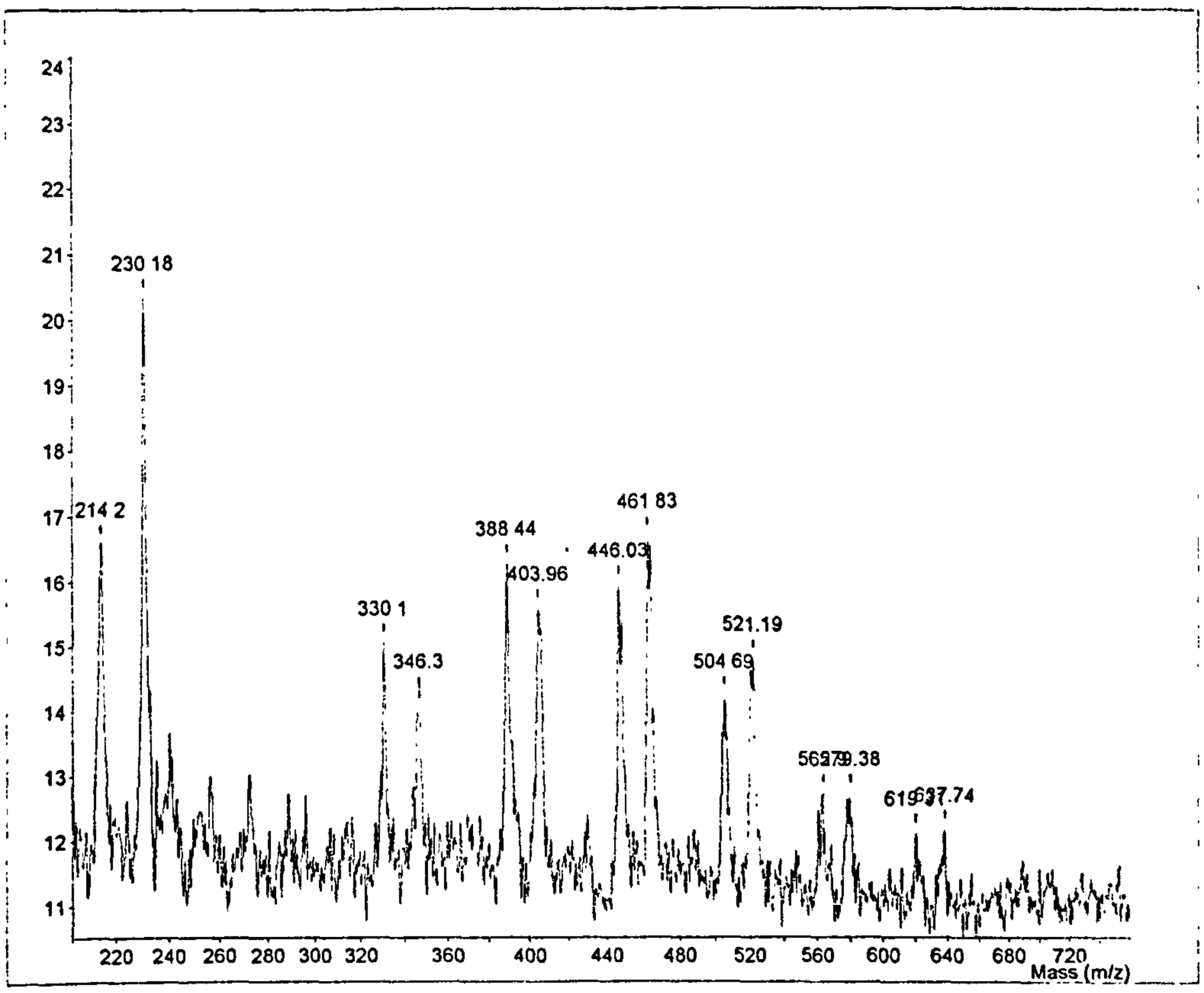
The MALDI detected three oligomers of decreasing abundance, none of which were noted in the MALDI spectrum of the liquid polyol sample (Figure 4.4). These peaks were calculated as cyclic oligomers (see Table 4.3) similar to those detected by Lawson et al using LC-MS[64].

Table 4.3: MALDI mass spectrum of the cured wet components of sample TC1 extracted in water

Cyclic oligomer	Mass	MALDI peak	- Na cation
AA-DEG | | DEG-AA	432.44	455.44	432.50
AA-DEG-AA | | DEG-AA-DEG	648.66	672.01	649.02
AA-DEG-AA-DEG | | DEG-AA-DEG-AA	864.88	887.96	864.97

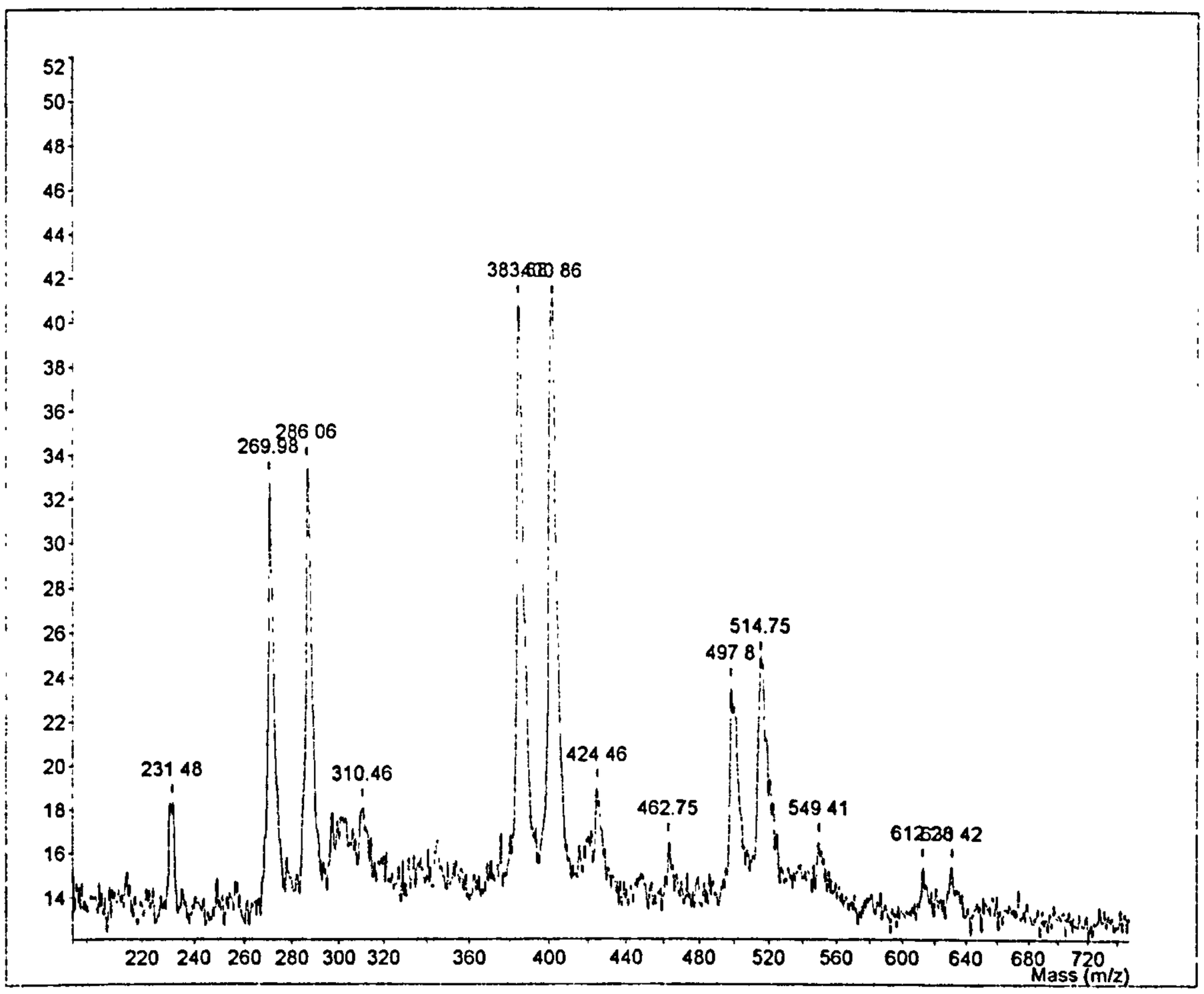
The lack of these peaks in the original mass spectrum of the liquid polyol component may be explained by the absence and subsequent formation during formulation. Although it is more likely to be that the cyclic oligomers are at a low concentration in comparison with the levels of linear oligomers and were masked by the more abundent linear oligomers in the liquid polyol spectrum. Once these linear oligomers react with the isocyanate component the cyclic species are left free to migrate and be detected by the MALDI-MS.

Figure 4.12: MALDI mass spectrum of urethane sample TC2 cured on aluminium foil and extracted in water



The MALDI detected six oligomers 58 units apart indicating the presence of polypropylene glycol. The initiator was calculated as propylene glycol. Hence this one component polyurethane system is based on a difunctional polypropylene glycol polyether.

Figure 4.13: MALDI mass spectrum of urethane sample TC3 cured on aluminium foil and extracted in water

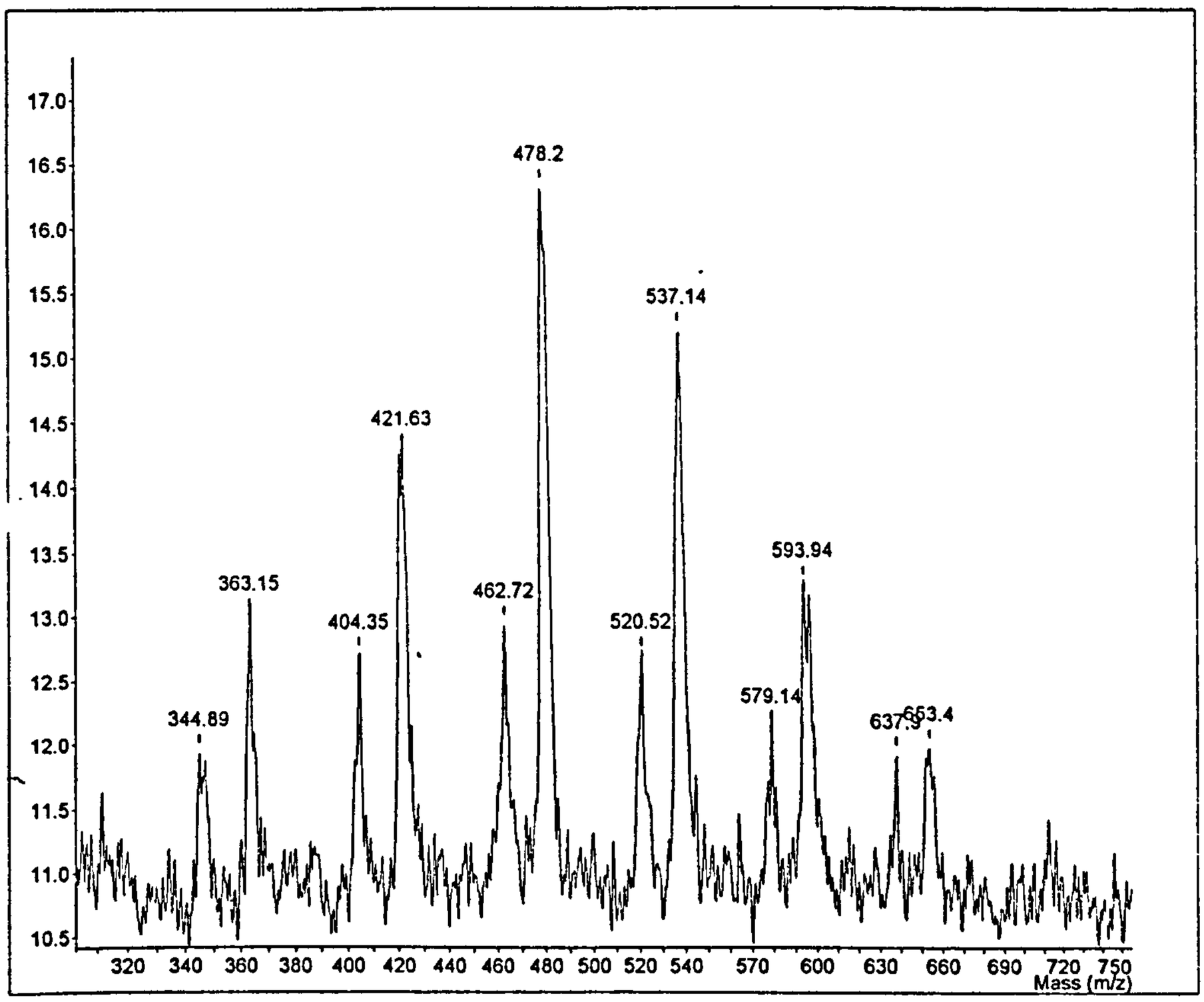


The MALDI detected four oligomers in the extract component as detailed in Table 4.4.

Table 4.4: MALDI mass spectrum peaks of urethane sample TC3 cured on aluminium foil and extracted in water

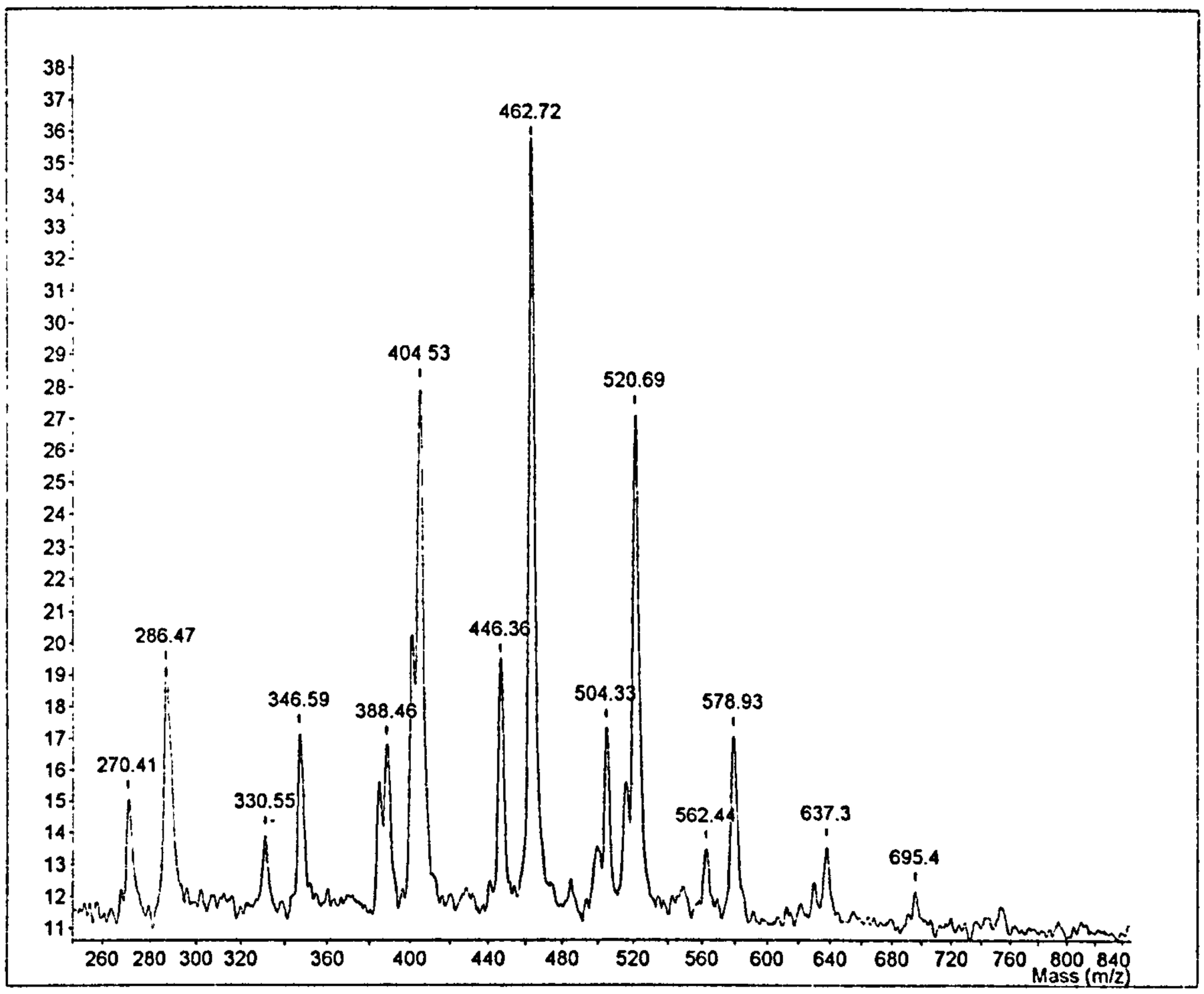
Oligomer	Mass	MALDI peak	-Na cation	MALDI peak	-K cation
TRI(CAP)	247.36	269.98	246.99	286.06	246.97
$TRI(CAP)_2$	360.52	383.88	360.89	400.86	361.77
$TRI(CAP)_3$	473.68	497.80	474.81	514.75	475.66
$TRI(CAP)_4$	586.84	612.28	589.29	630.42	591.33

Figure 4.14: MALDI mass spectrum of urethane sample 1 cured on aluminium foil and extracted in water



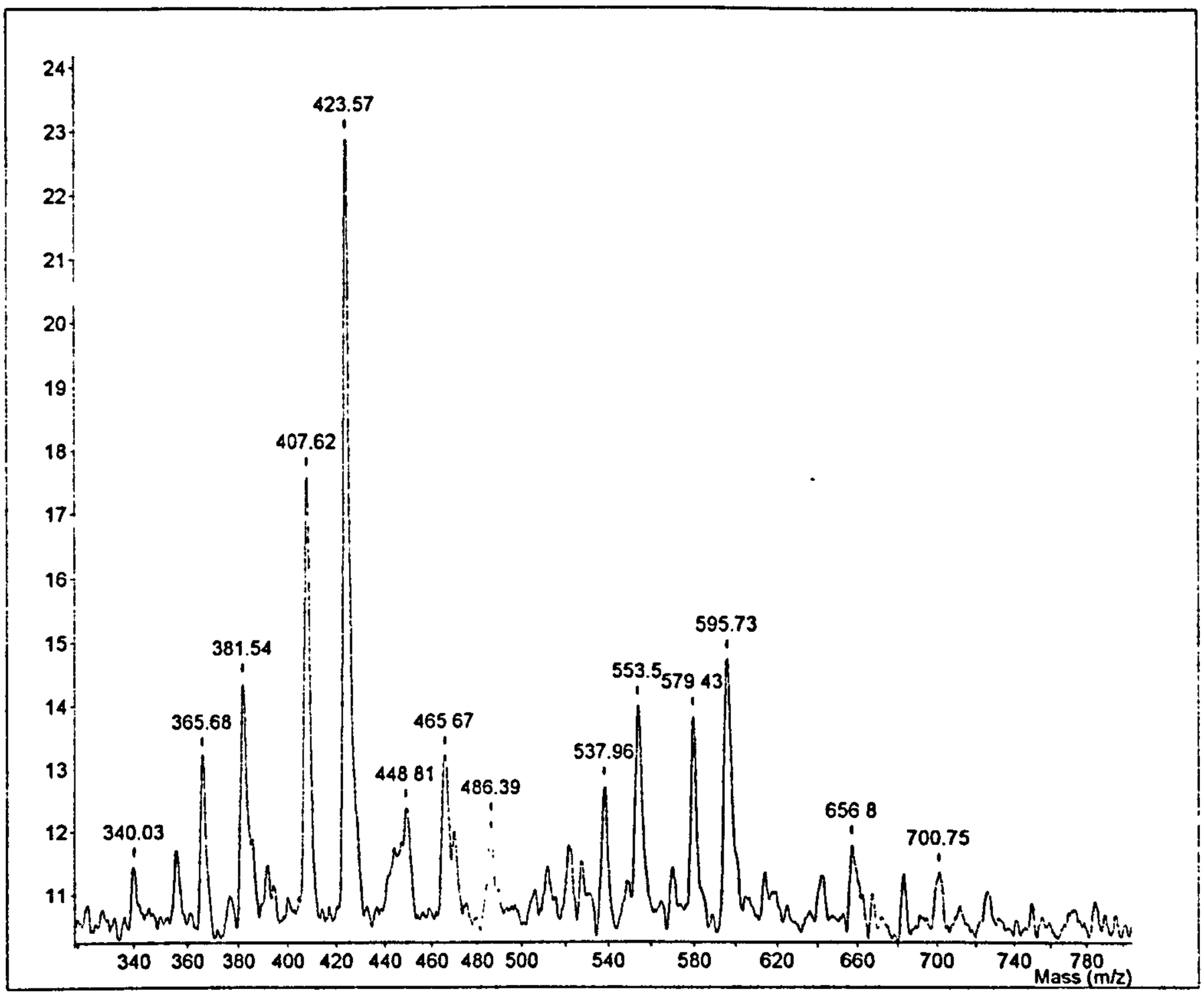
From the cured adhesive extract the MALDI detected the presence of six polypropylene glycol oligomers also found in the liquid polyol component (see Figure 4.7). This polyol appears to be a trifunctional polyether system as when n = 1, its mass is 76 corresponding with trifunctional glycerol.

Figure 4.15: MALDI mass spectrum of urethane sample 2 cured on aluminium foil and extracted into water



The MALDI detected the lower distribution of polyol peaks shown in the spectrum of the liquid polyol component in ethyl acetate (c.f. Figure 4.8). None of the oligomers in the higher polyol distribution were detected. In all eight oligomer peaks were observed corresponding to polypropylene glycol based on propylene glycol as the initiator.

Figure 4.16: MALDI mass spectrum of sample 3 cured on aluminium foil and extracted into water



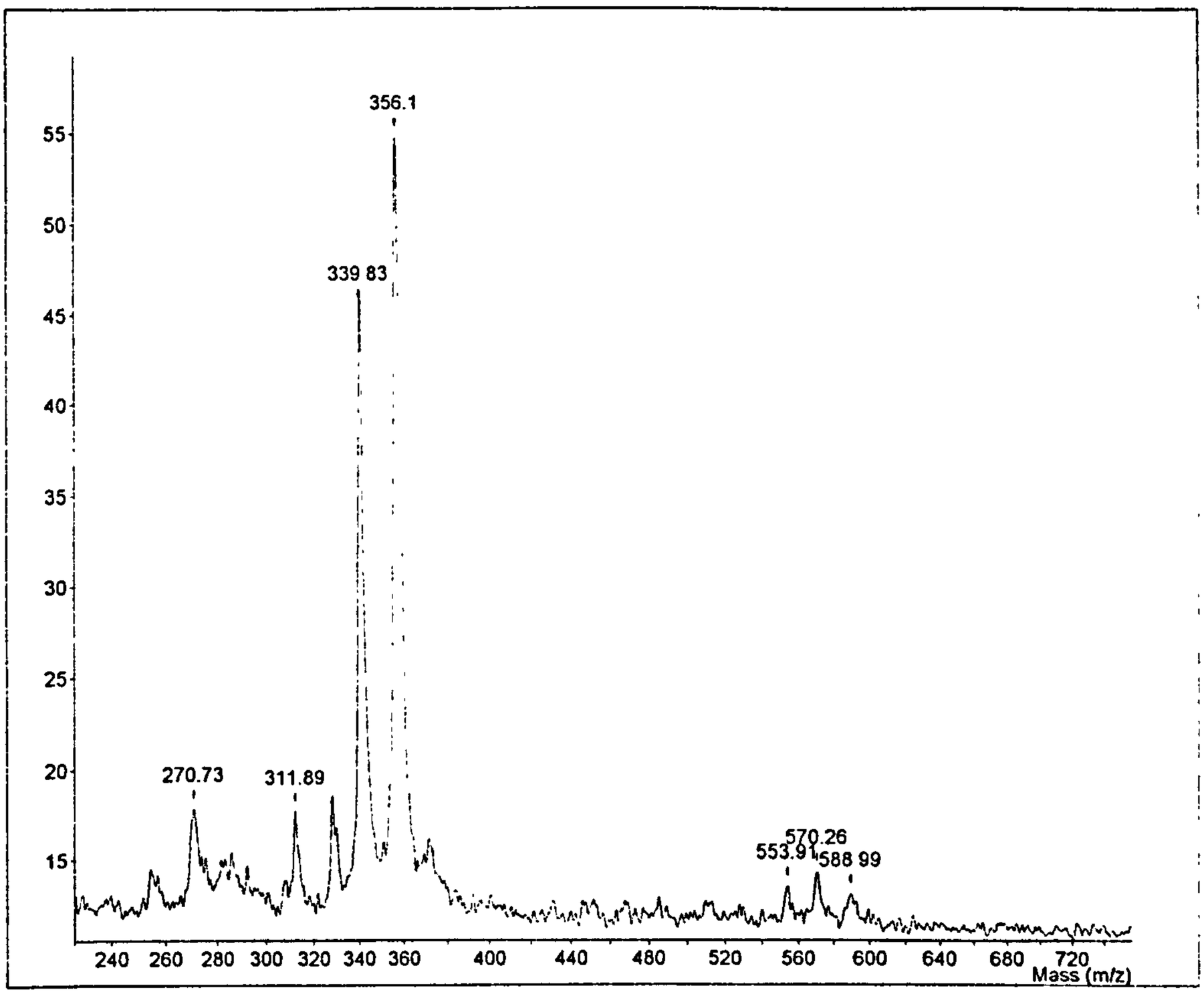
The MALDI of this polyester system again produced peaks not noted in the spectrum of the liquid sample and again they were assigned as cyclic oligomers using various combinations of the reactants deduced from the liquid polyol spectra. These reactants are adipic acid (AA), ethylene glycol (EG) and neopentyl glycol (NPG), the cyclic oligomer combinations are outlined in Table 4.5.

Table 4.5: MALDI mass spectrum peaks of the cured urethane sample 3 extracted into water

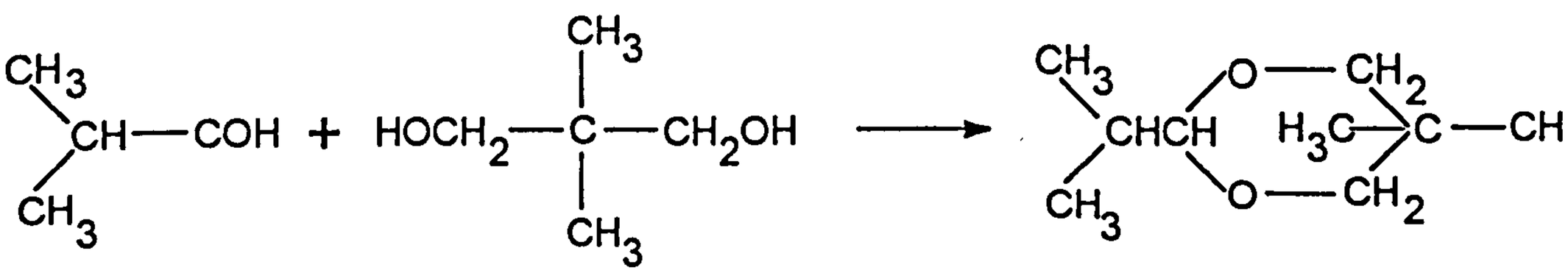
Oligomer	Mass	MALDI peak	-Na cation	MALDI peak	-K cation
AA-EG EG-AA	344.34	367.68	344.69	383.54	344.44
AA-EG NPG-AA	386.42	409.62	386.63	425.57	386.47
AA-NPG NPG-AA	428.30	450.81	427.82	467.67	428.57
AA-EG-AA EG-AA-EG	516.51	539.96	516.97	555.50	516.40
AA-EG-AA EG-AA-NPG	558.59	581.43	558.44	597.73	558.63

The MALDI produced a number of peaks within a small mass range which complicated the process of identifying them as it was difficult to define which were molecular ion peaks and which were sodium and potassium cation peaks. This indicates the number of combinations possible when a polyester has been formulated with more than one polyfunctional carboxylic acid or glycol. One way to overcome this problem of identifying the form in which a molecule is represented is to spike the sample with another salt. For example in these investigations, where the peak nature was unknown, the samples were spiked with caesium chloride, which was mixed in with the matrix solution and resulted in the detection of single peaks 132 units higher than previously noted in the form of caesium cations.

Figure 4.17: MALDI-MS of urethane sample 4 cured on foil and extracted into water



This produced two large peaks at 339 and 356 also noted in the liquid polyol spectra, believed to be sodium and potassium derivatives of the same molecule, which will have a molecular ion mass of 316. This could be an additive in the polyurethane system or a reaction by-product of the neopentyl glycol. Neopentyl glycol is prepared from isobutyraldehyde (IBA) and formaldehyde. These starting materials can reform under acid conditions, i.e. the conditions of the polyurethane reaction, the IBA may then react with the neopentyl glycol as follows:



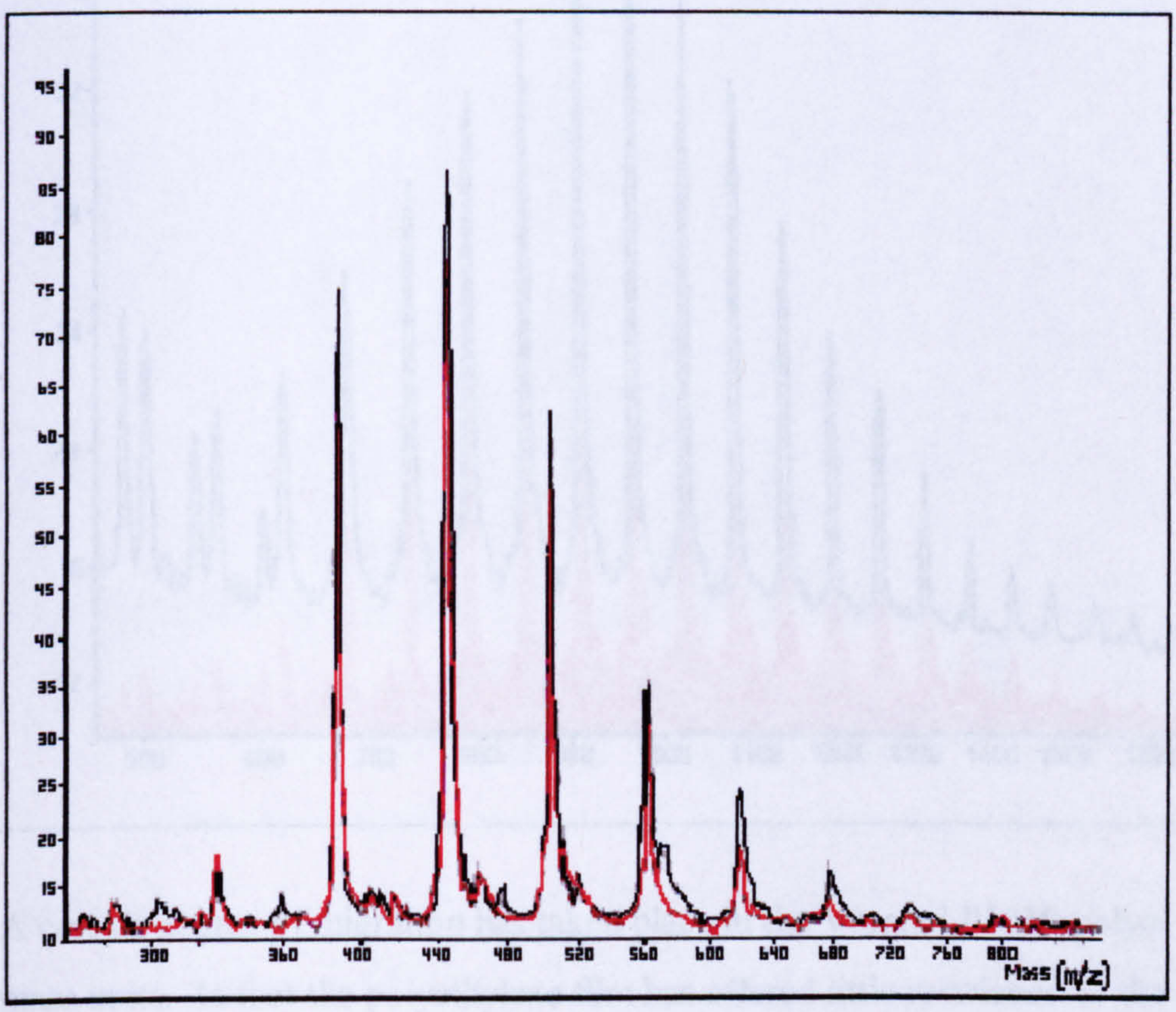
IBA Neopentyl glycol

This product has a very pungent odour at ppb levels and the dimer has a mass of 316.

4.3.1.3 Migration of liquid polyol through polyethylene film

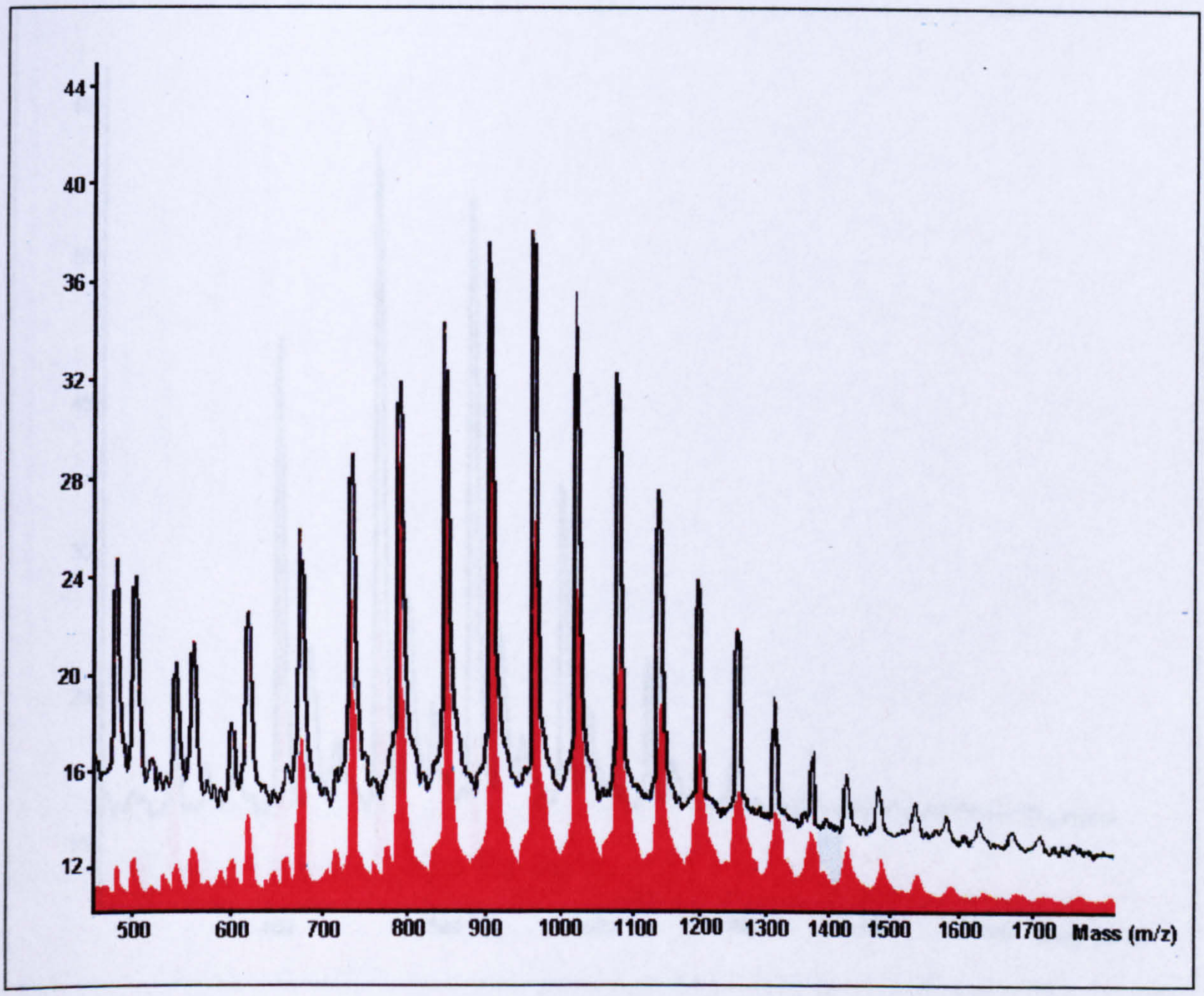
The MALDI spectrum from the pouch migrant was compared to the mass spectrum of the liquid polyol sample, to determine the extent of polyol migration through 45 μm polyethylene film.

Figure 4.18: MALDI mass spectrum of liquid Voranol P400 in ethyl acetate and after migration through 45 μm polyethylene film



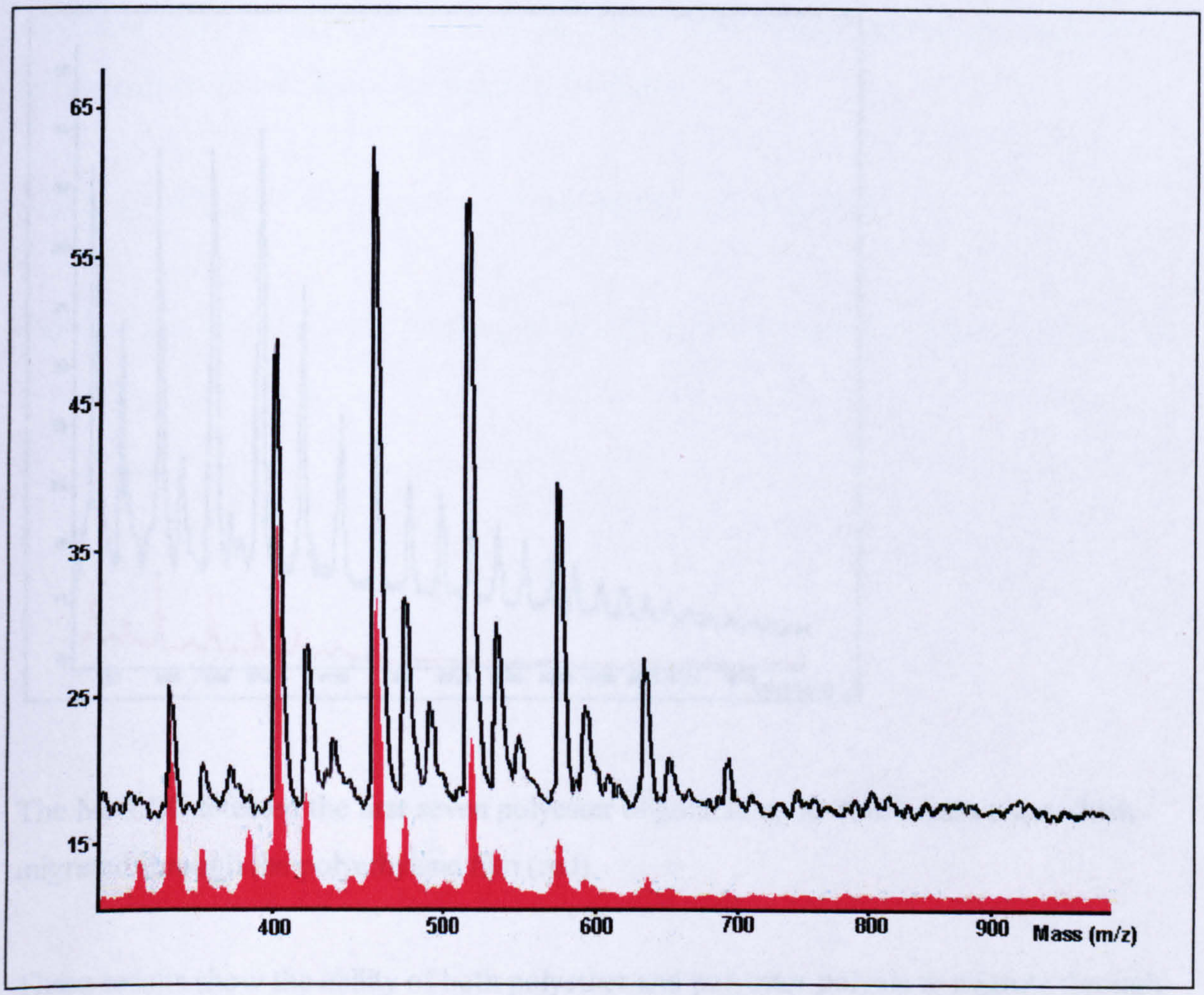
The MALDI spectrum is identical to that of the liquid Voranol P400 in ethyl acetate (black). All seven oligomers were detected which indicates that the polyethylene film offers no selective barrier to the difunctional polypropylene glycol of a mean molecular weight of 400 mass units. This led to the analysis of the longer chain Voranol P1010 sample.

Figure 4.19: MALDI mass spectrum of liquid Voranol P1010 in ethyl acetate and after migration through 45 μm polyethylene film



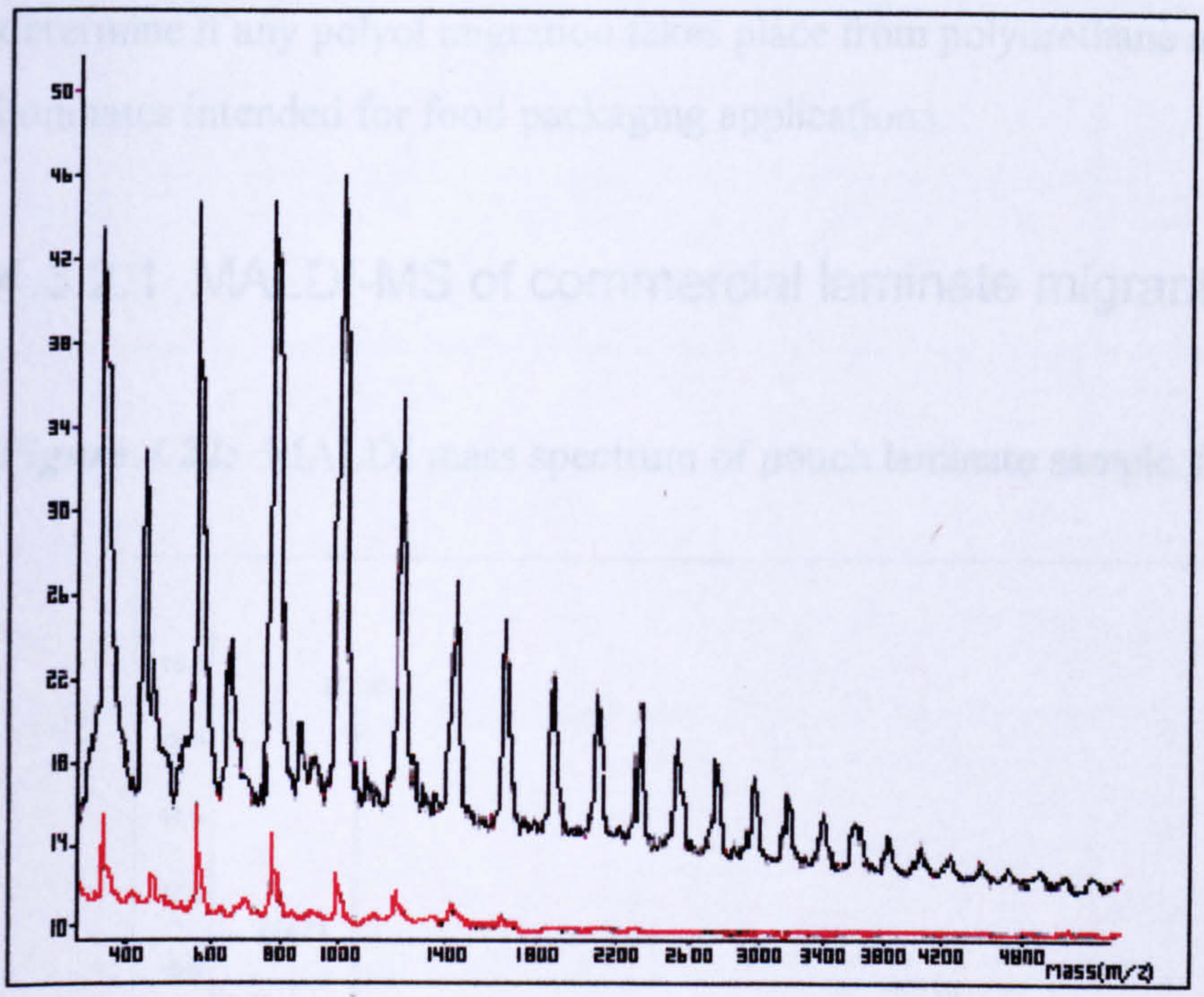
A certain degree of migration has taken place in the Voranol P1010 polyol up to 1,500 mass units. In fact the polyethylene film has offered little restriction to the migration of this difunctional polypropylene glycol (red). The migration of a trifunctional polypropylene was then checked to see if the difference in polyether structure would effect its ability to migrate through the polyethylene film.

Figure 4.20: MALDI mass spectrum of liquid polyol sample 1 in ethyl acetate and after migration through 45 μm polyethylene film



The MALDI spectrum shows a degree of selectivity from the polyethylene film. Five of the lowest molecular weight oligomers have migrated (red), whereas in the liquid mass spectrum seven oligomers were detected. This shows that the polyethylene film is a selective barrier to this trifunctional polypropylene glycol, probably due to its bulkier structure.

Figure 4.21: MALDI mass spectrum of liquid polyol sample TC1 in ethyl acetate and after migration through 45 μm polyethylene film



The MALDI detected the first seven polyester oligomers up to 1,500 mass units which migrated through the polyethylene film (red).

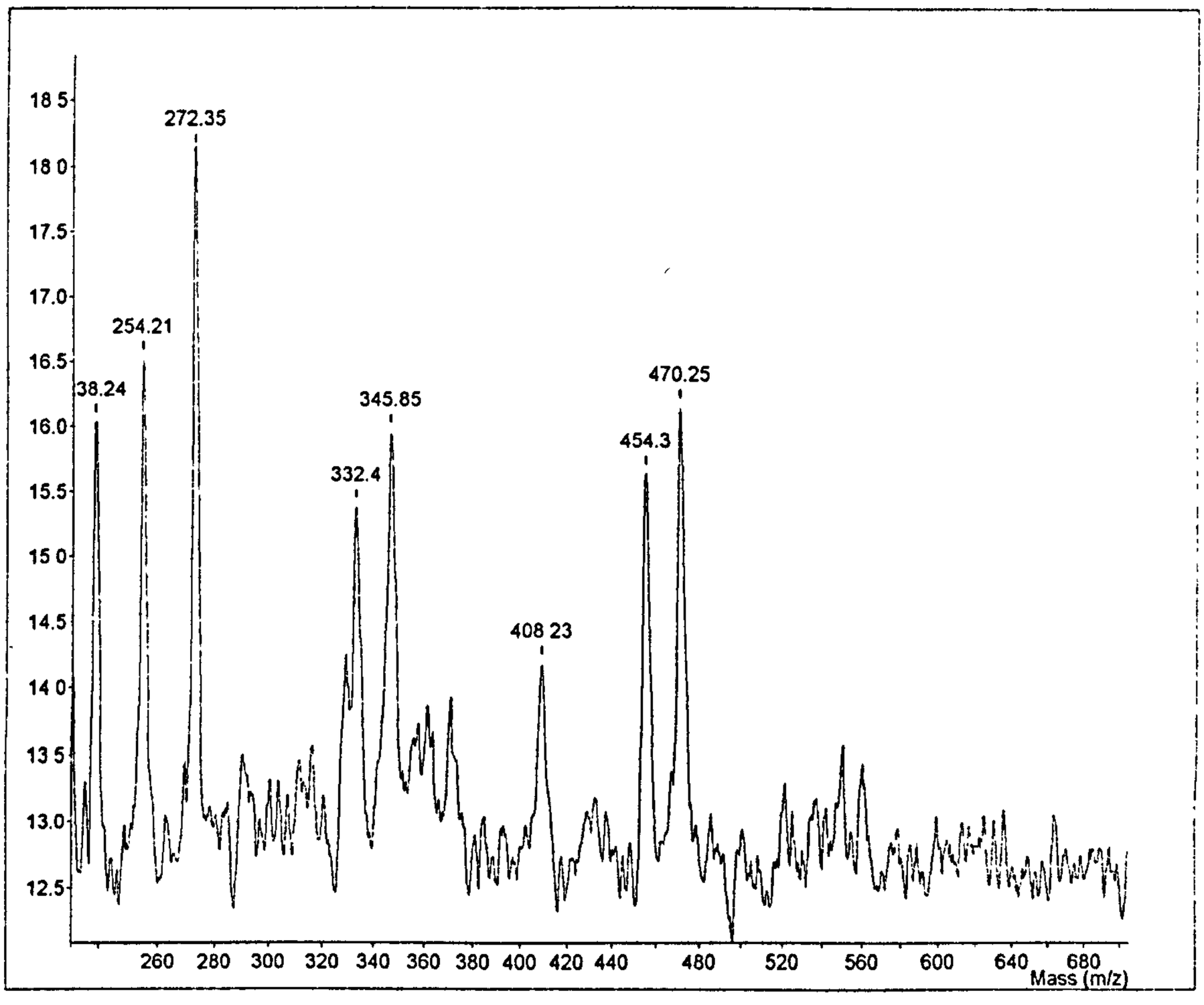
These results show the ability of both polyether and polyester polyols to migrate through polyethylene film, which is the most common plastic used in commercial laminates. It is used as the inner layer due to its excellent heat sealing properties and as such will come into direct contact with the foodstuff. Thus there is the potential for polyol migration into the foodstuff.

4.3.2 Analysis of commercial laminate samples

Analytical work was then carried out on extracts from pouches of commercial laminates to determine if any polyol migration takes place from polyurethane adhesives in commercial laminates intended for food packaging applications.

4.3.2.1 MALDI-MS of commercial laminate migrants

Figure 4.22: MALDI mass spectrum of pouch laminate sample TC1 migrants into water



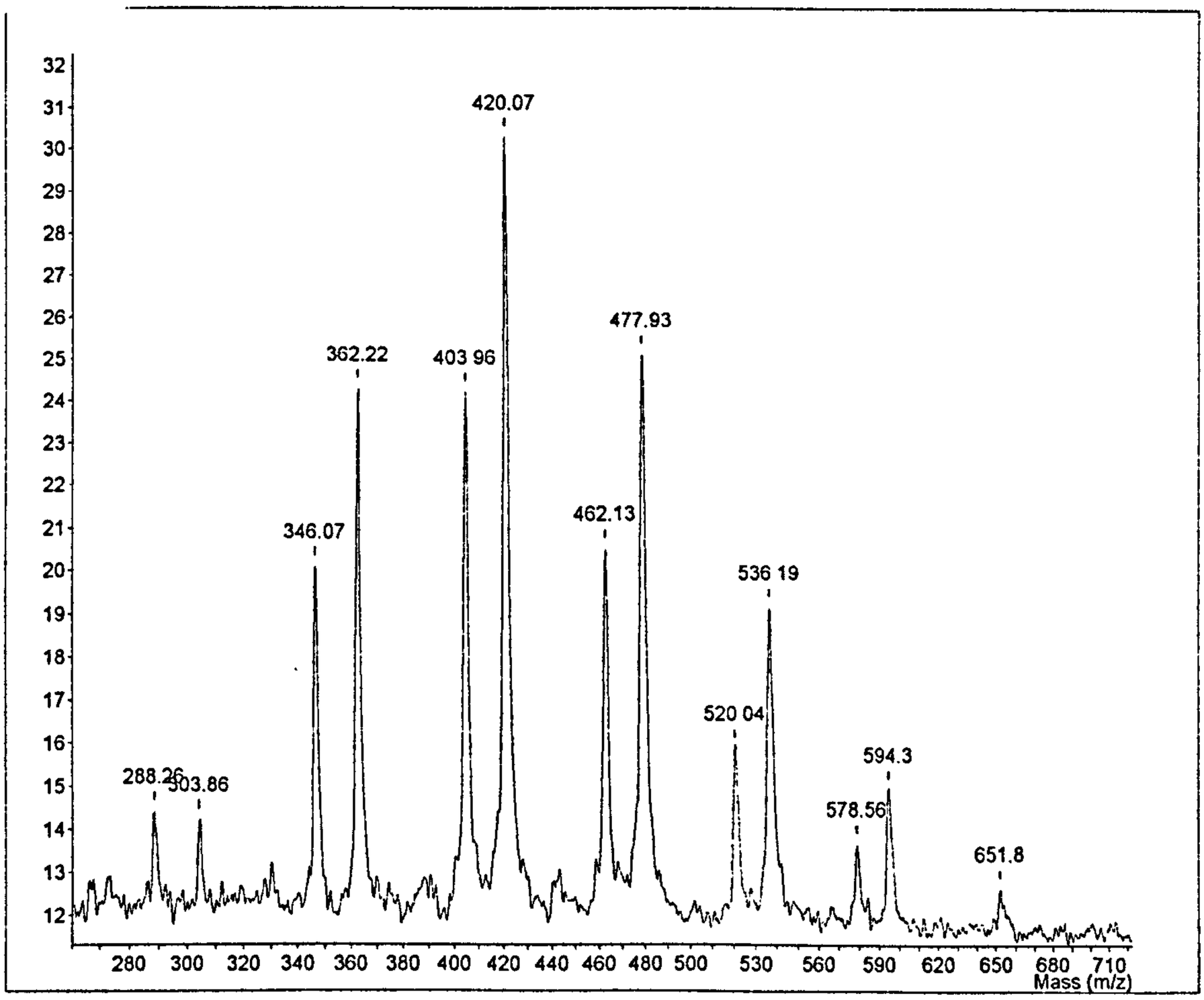
Six peaks were detected by the MALDI and calculated as polyester oligomers, detected as sodium and potassium cations (Table 4.6).

Table 4.6: MALDI mass spectra peaks and corresponding polyol peaks of sample TC1 laminate pouch extracted in water

Oligomer	Mass	MALDI peak	- Na cation	MALDI peak	- K cation
AA-DEG	216.22	239.9	216.91	256.04	216.95
AA-DEG	234.24	256.04	233.05	274.35	235.26
AA-DEG DEG-AA	432.44	455.77	432.78	472.23	433.14

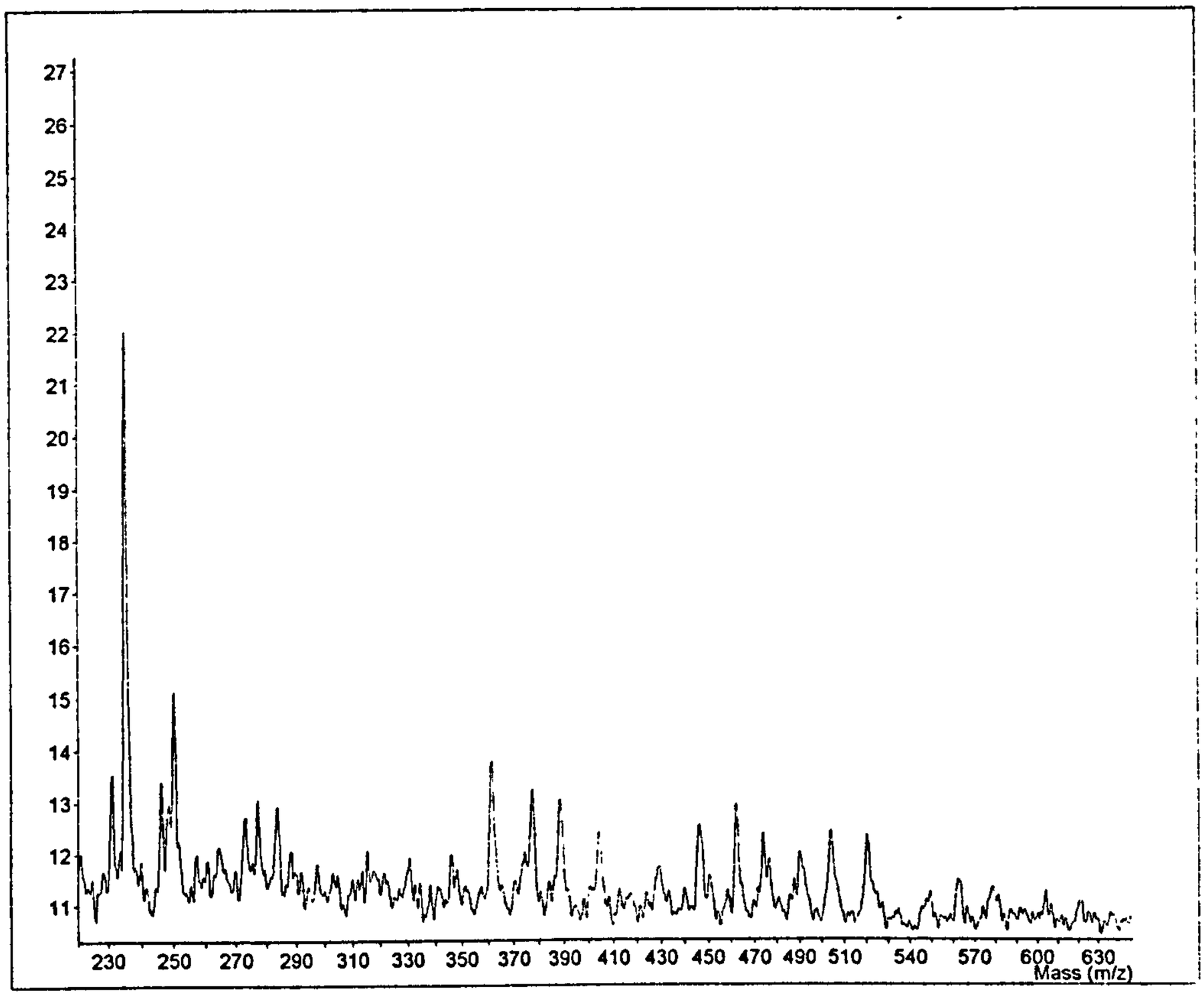
MALDI analysis of laminate pouches of samples TC2 and TC3 were not possible due to lack of laminate sample.

Figure 4.23: MALDI mass spectrum of pouch laminate sample 1 extracted in water



The MALDI detected seven polyether oligomers, separated by 58 mass units, as both sodium and potassium cations.

Figure 4.24: MALDI mass spectrum of pouch laminate sample 2 extracted in water



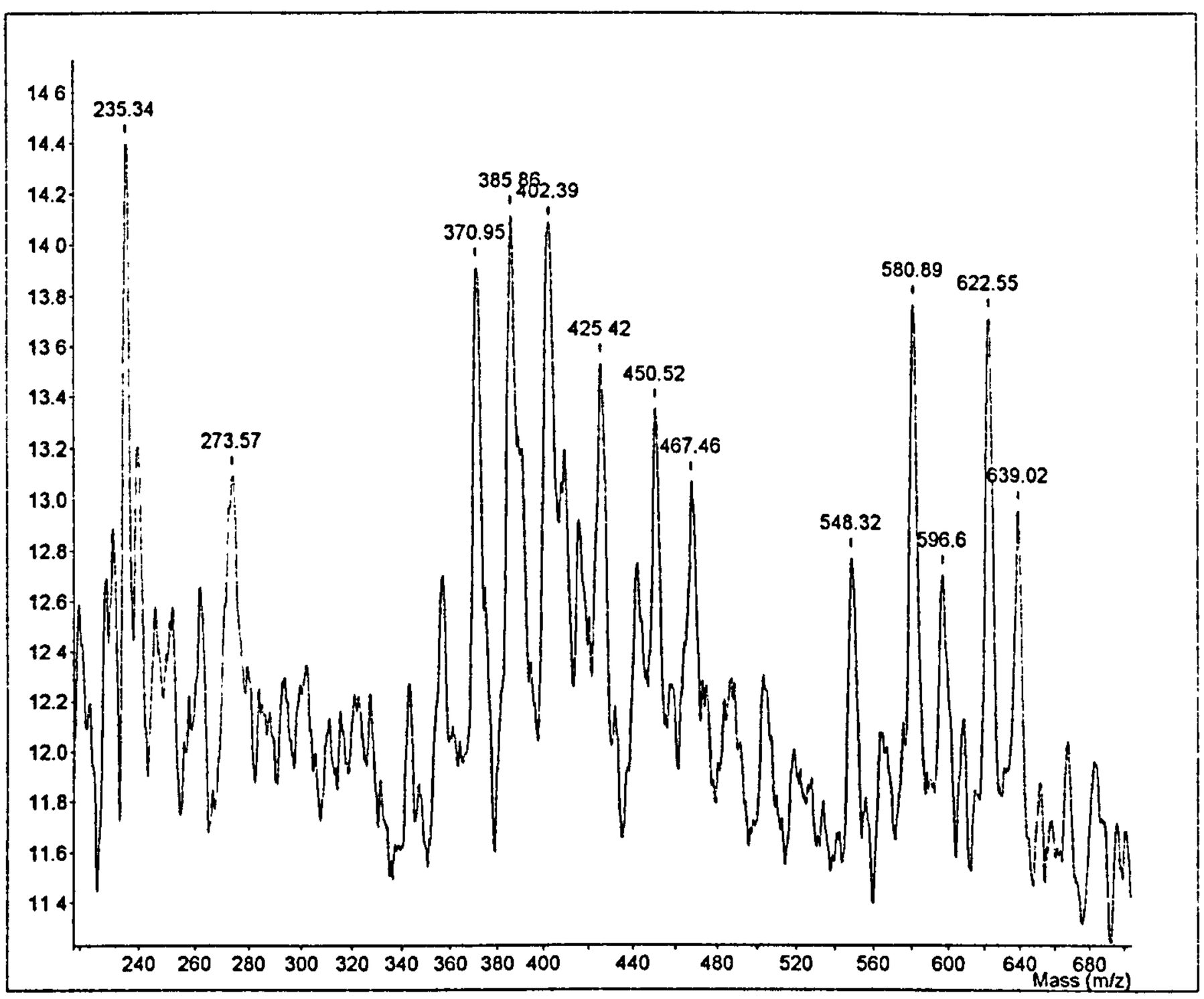
A number of peaks detected by the MALDI also appear in the liquid polyol spectrum.

Table 4.7: MALDI peaks of sample 2 pouch migrants and possible polyol oligomers

Oligomer	Mass	MALDI peak	- Na cation	MALDI peak	- K cation
		236.84	213.85	251.82	212.72
		362.99	340.00	378.97	339.87
$H[PO]_6OH$	366.50	389.92	366.93	405.95	366.85
$H[PO]_7OH$	424.58	447.78	424.79	464.14	425.04
$H[PO]_8OH$	482.66	505.86	482.87	522.04	482.94
$H[PO]_9OH$	540.74	563.58	540.59	580.29	541.19

From the migrant peaks three have been identified as polypropylene glycol peaks. The other migrants may be additives from either the adhesive or polyethylene inner layer.

Figure 4.25: MALDI mass spectrum of pouch laminate sample 3 extracted in water



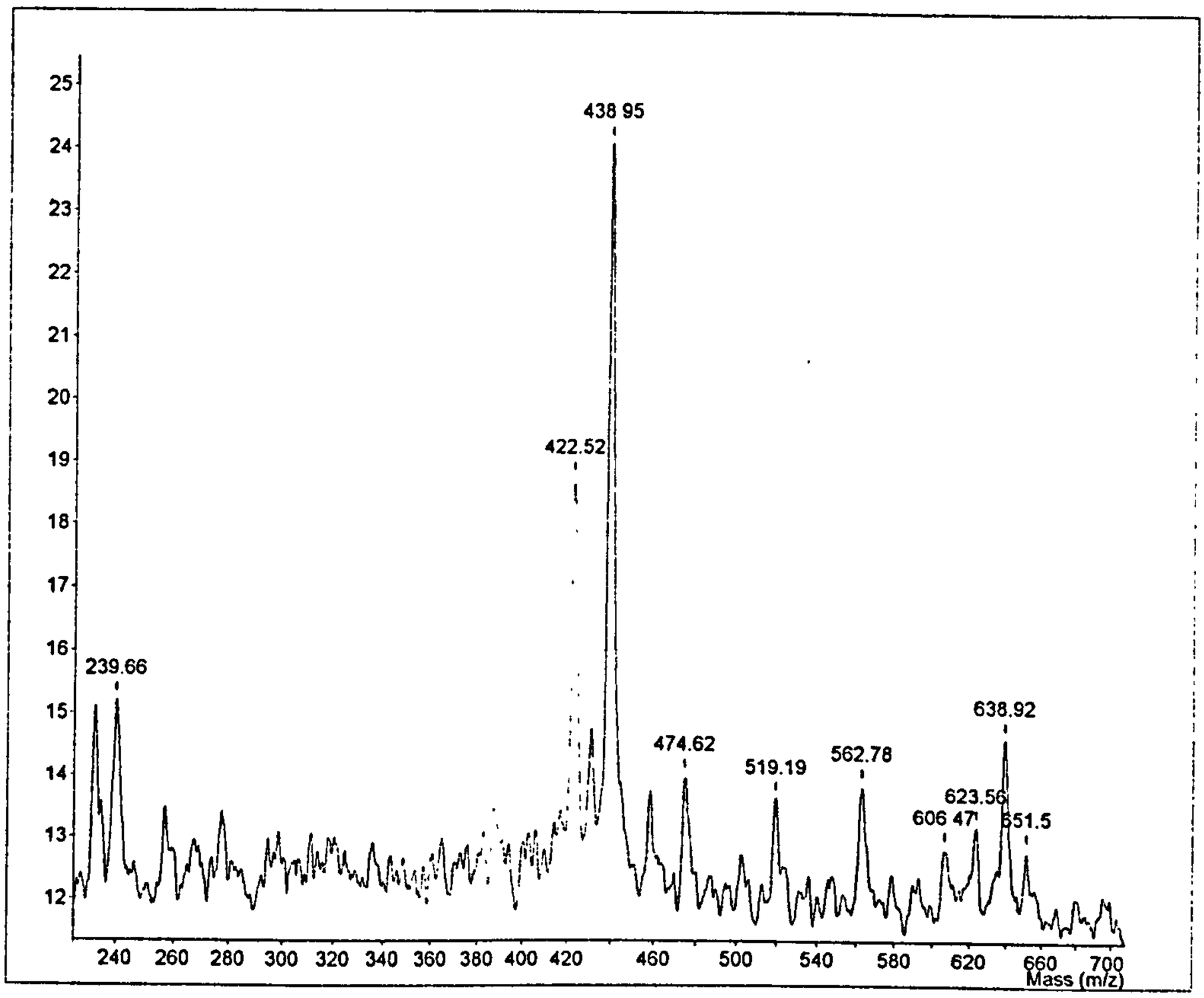
A number of peaks were detected by the MALDI which correspond to the peaks noted in the MALDI mass spectrum of the cured adhesive extract and detailed in Table 4.8.

Table 4.8: MALDI mass spectrum peaks of water extracted for laminate pouch sample 3 with possible polyol oligomers

Oligomer	Mass	MALDI peak	- Na cation	MALDI peak	- K cation
AA-EG EG-AA	344.34	370.95	347.96	385.86	346.76
AA-NPG EG-AA	386.42	404.39	381.4	425.42	386.32
AA-NPG NPG-AA	428.50	452.52	429.53	467.46	428.36
AA-EG-AA EG-AA-NPG	558.51	582.89	559.9	598.60	559.5
AA-NPG-AA EG-AA-NPG	600.67	622.55	599.56	639.02	599.92

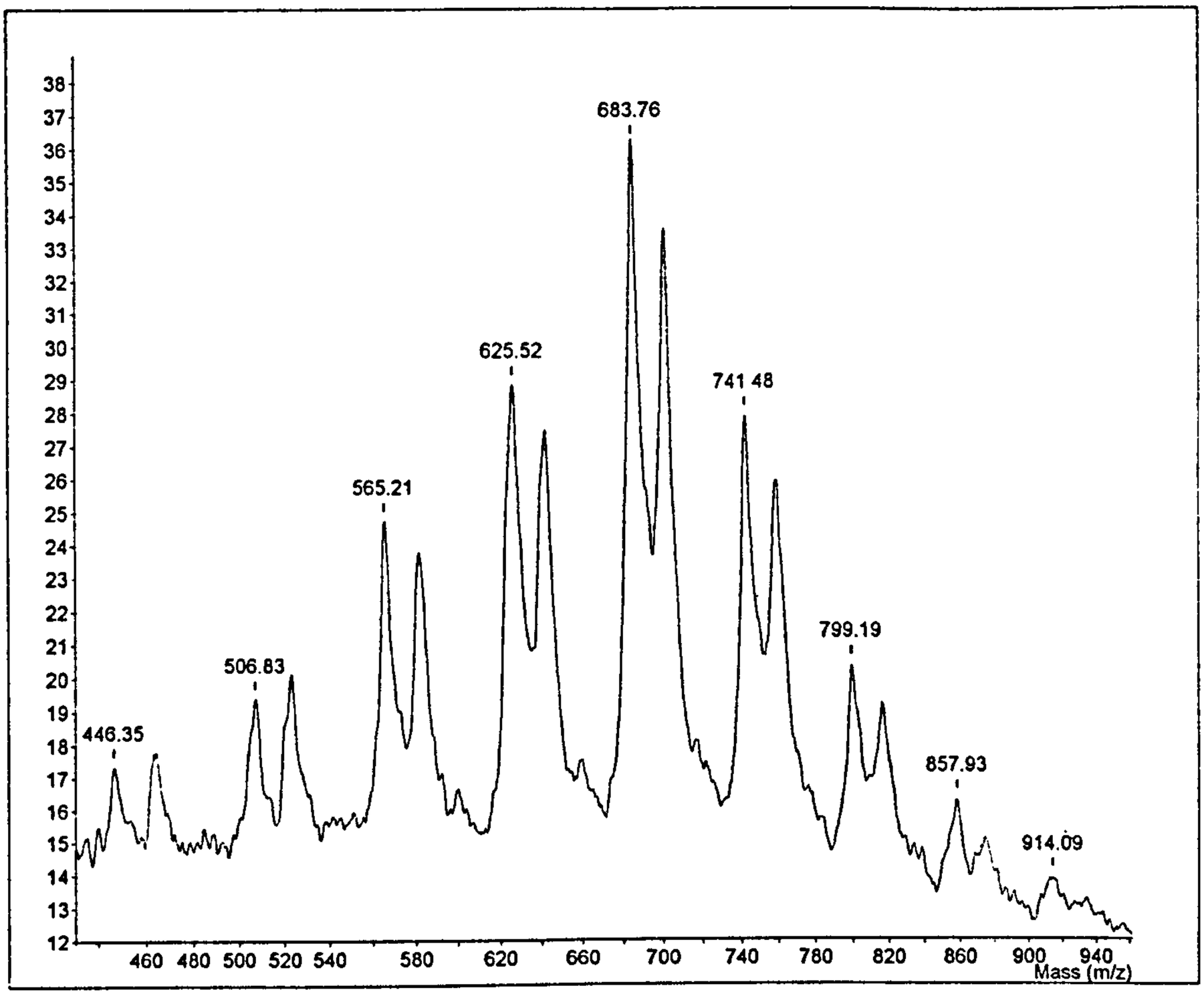
Five oligomers were detected in the pouch residue, all of which correspond to the mass units of various cyclic oligomers derived from adipic acid (AA), diethylene glycol (DEG) and neopentyl glycol (NPG). Again these cyclic oligomer combinations were not noted in the mass spectrum of the liquid polyol sample.

Figure 4.26: MALDI mass spectrum of pouch laminate samples 4 and 5 extracted in water



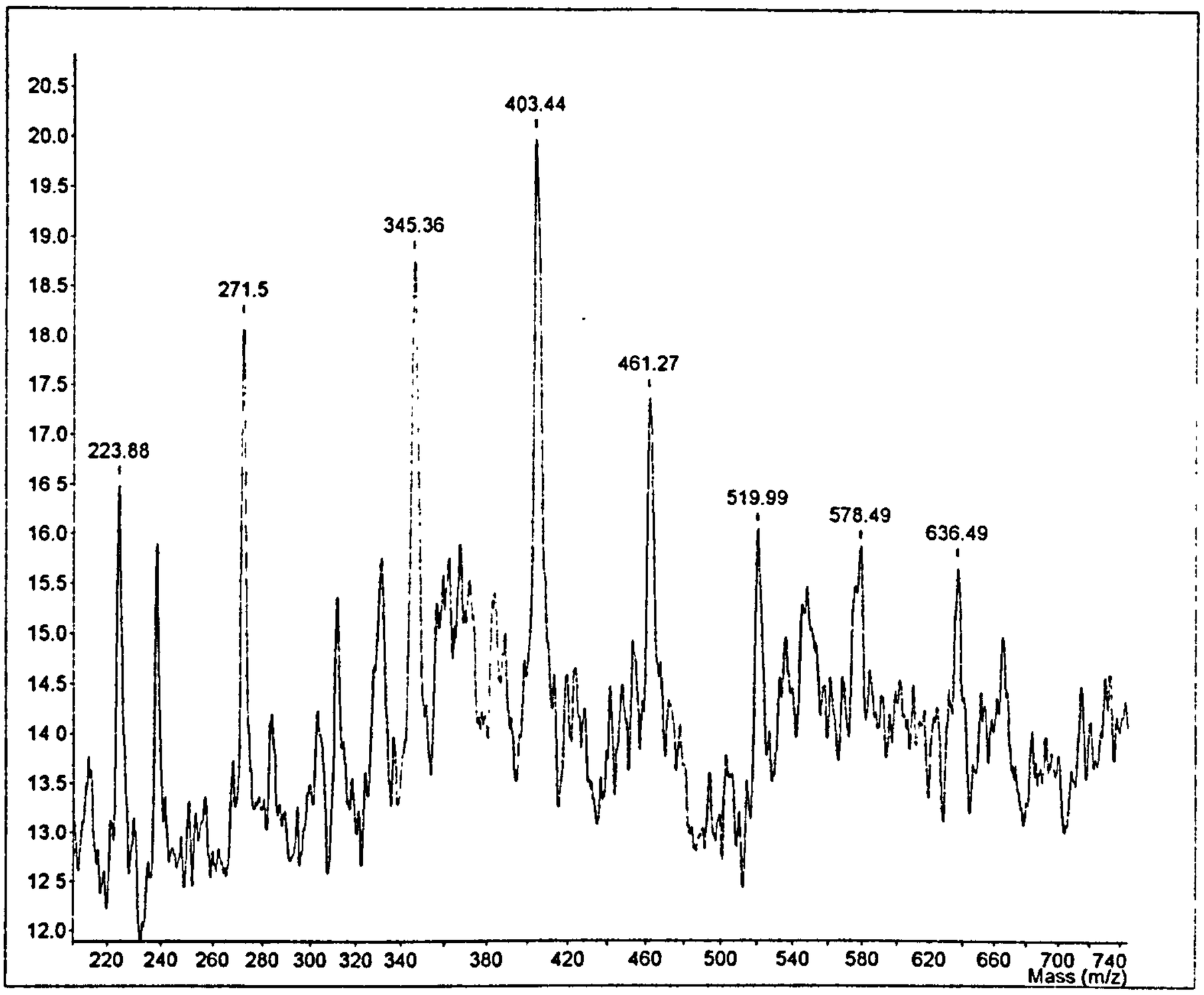
The MALDI mass spectrum detected two large peaks, sodium and potassium forms of the same molecule with a molecular weight of 400. This does not correspond to any cyclic polyester oligomer masses and so may be due to an additive migrant from either the adhesive or polyethylene inner film.

Figure 4.27: MALDI mass spectrum of pouch laminate sample JSD extracted in water



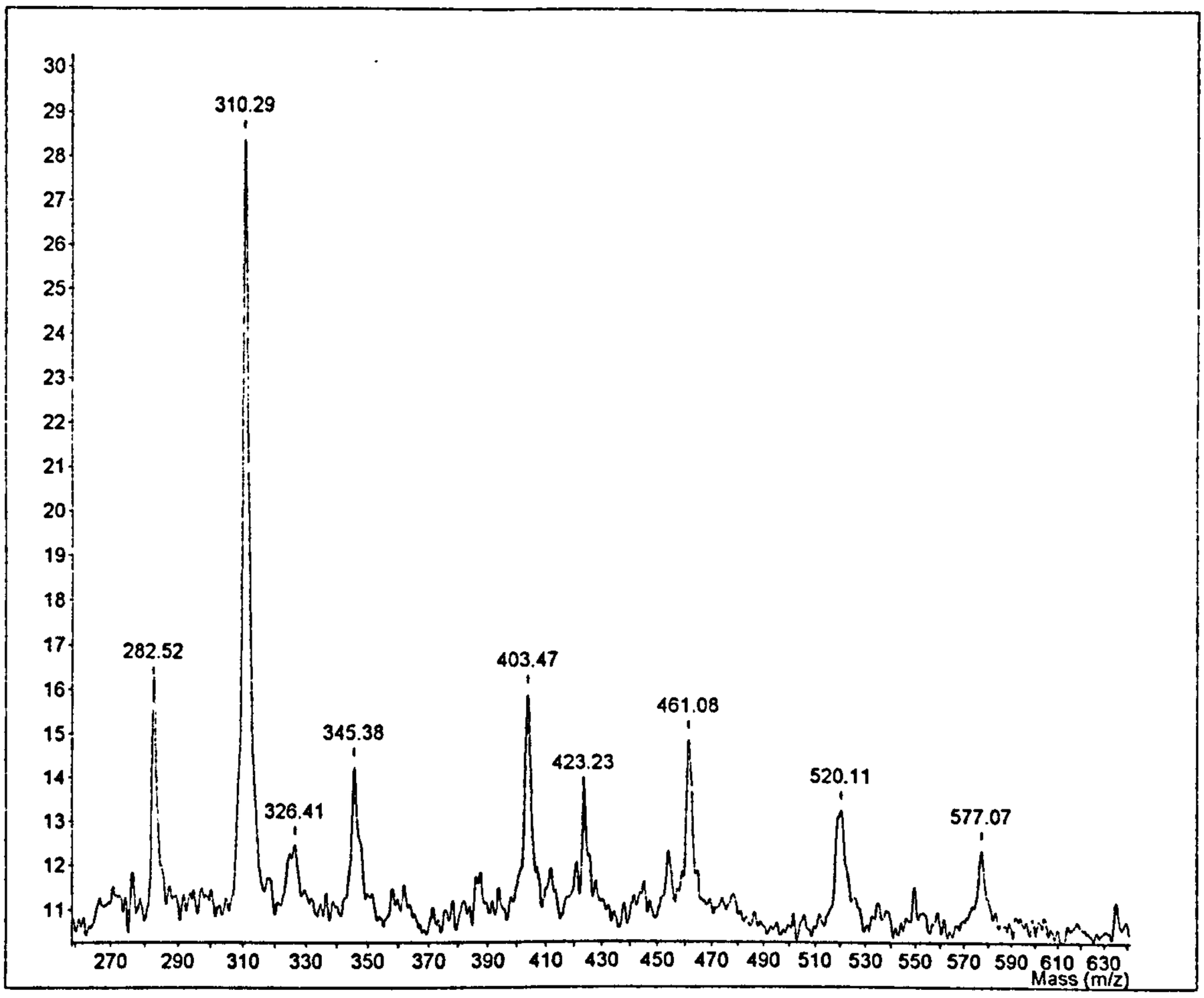
Nine oligomers were detected in the pouch extract 58 mass units apart corresponding to polypropylene glycol. The initiator was calculated to be propylene glycol. Hence this is a difunctional polypropylene glycol polyether based polyurethane adhesive system. This polyol distribution corresponds to the spectrum of the generic Voranol P400 polyol.

Figure 4.28: MALDI mass spectrum of pouch laminate sample Z extracted in water



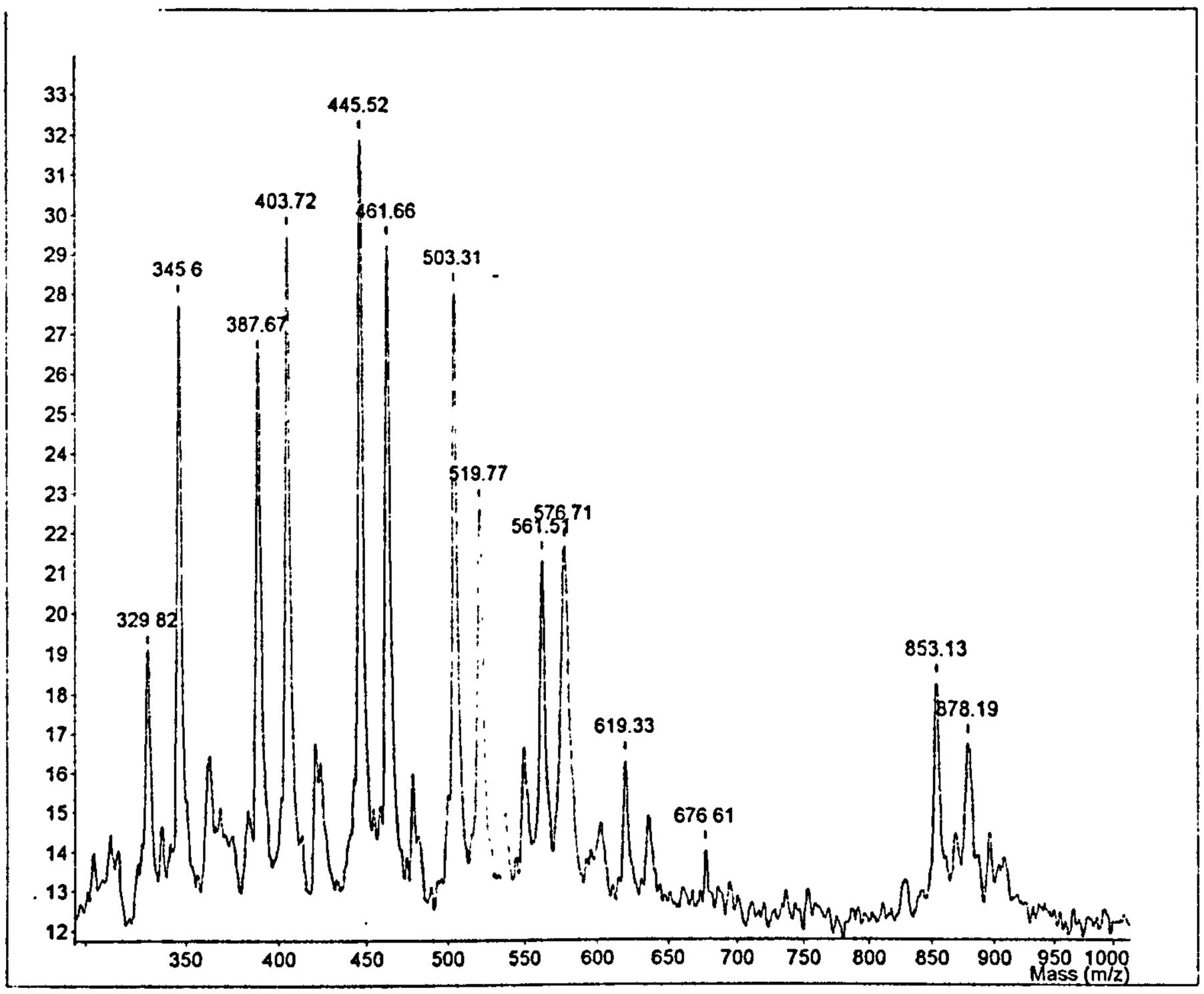
Six of the detected MALDI peaks are 58 mass units apart which corresponds to polypropylene glycol. The initiator was then calculated as glycerol, so this is a trifunctional polypropylene glycol based polyurethane adhesive system of the same mass distribution of the liquid polyol sample 1.

Figure 4.29: MALDI mass spectrum of pouch laminate sample 481 extracted in water



Five oligomers were detected by the MALDI all 58 mass units apart, indicating that propylene oxide is the repeat molecule. It was determined that this is a trifunctional polypropylene glycol polyether based on glycerol. Similar to the peaks detected in the spectrum of polyol 1.

Figure 4.30: MALDI mass spectrum of pouch laminate sample 484 extracted in water



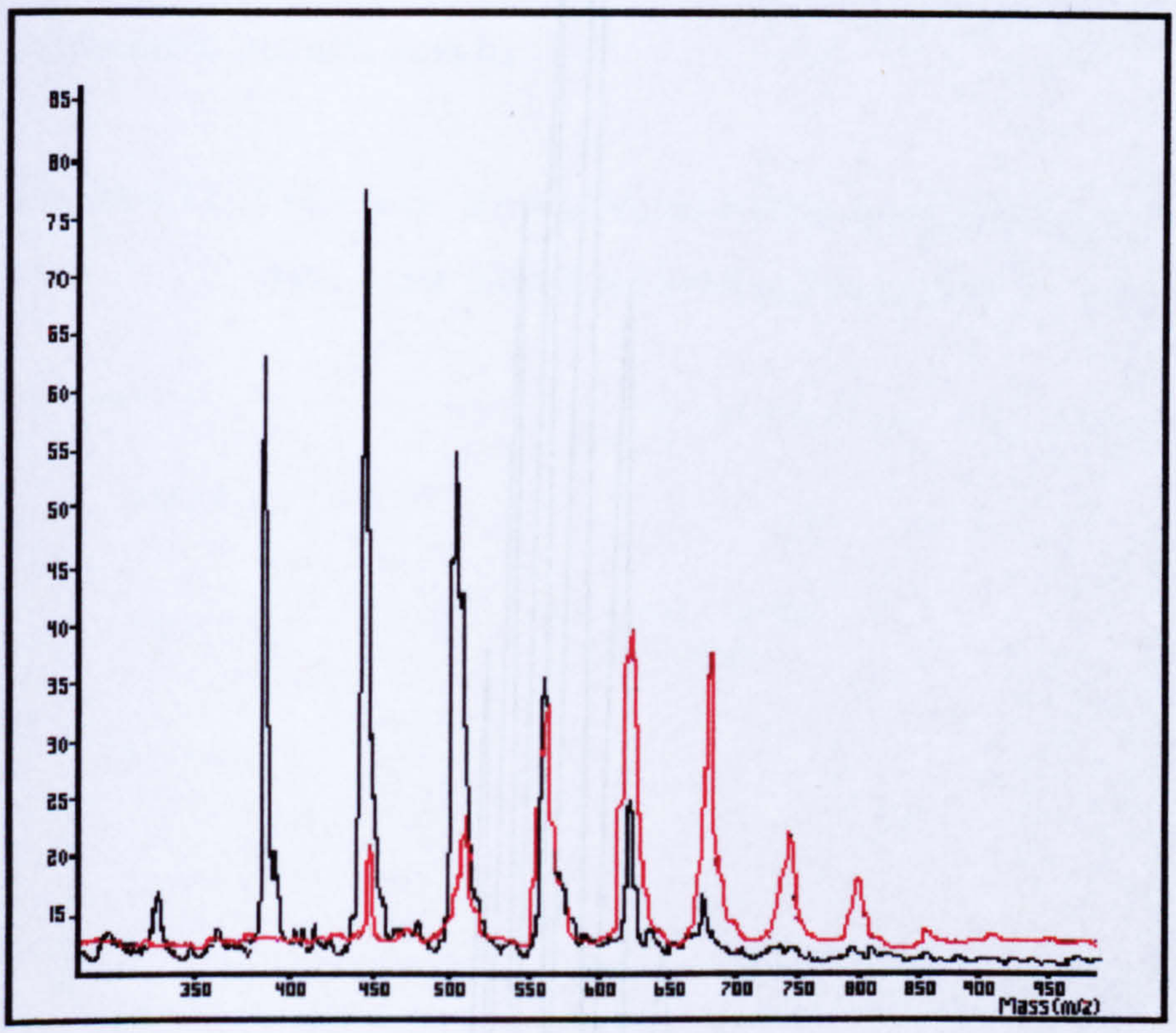
The MALDI mass spectrum detected a distribution of peaks between 330 and 675 mass units. Corresponding to a difunctional polypropylene glycol polyether, hence the adhesive used in the commercial laminate sample is polyether based.

4.3.2.2 Quantification of polyether migrants.

The MALDI-MS revealed the following samples were polyether based:- Samples 1, 2, Z, 481, 484 and JSD, and of these samples 2, 484 and JSD contain difunctional polypropylene glycol with a mass distribution around 400 and samples 1, Z and 481 are composed of trifunctional polypropylene glycol again with a mass distribution around 400, which are the liquid polyol samples Voranol P400 and polyol sample 1 respectively.

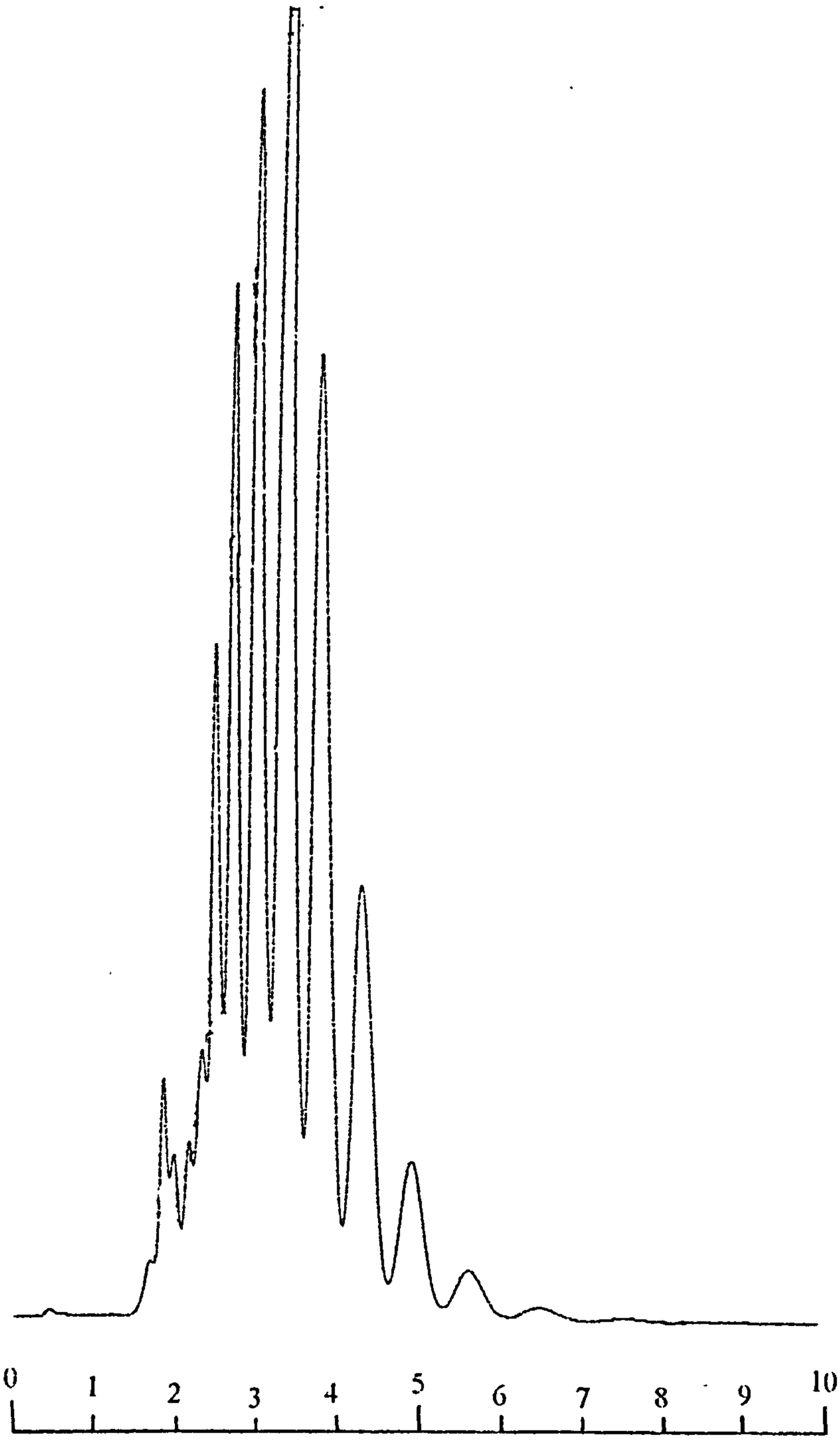
Calibration curves were determined for each of these liquid polyols after derivatisation with phenyl isocyanate and analysis by HPLC. In all cases after derivatisation of the sample it was run on the MALDI-MS to check that complete derivatisation is achieved and confirm the functionality of the polyol sample. The latter is checked by comparing the derivatised distribution with that of the polyol. If the distribution has shifted by 240 mass units it indicates the addition of two phenyl isocyanate units and thus each oligomer must have two hydroxyl groups and be difunctional, and a shift of 360 mass units to the right indicates the addition of three phenyl isocyanate units and so the polyol must be trifunctional. A comparison of these MALDI mass spectra is shown in Figure 4.31 with both the MALDI of the derivatised polyol and that of the liquid polyol diluted in ethyl acetate.

Figure 4.31: MALDI mass spectra of liquid Voranol P400 in ethyl acetate and the sample in acetonitrile after derivatisation with phenyl isocyanate.



The MALDI shows the expected shift of 240 mass units (red) and so confirms that this is a difunctional polypropylene glycol sample. It also indicates that the reaction is complete as no peaks are detected in the original peak distribution region of the mass spectrum. This complete derivatisation led to the analysis of the Voranol P400 by HPLC (Figure 4.32).

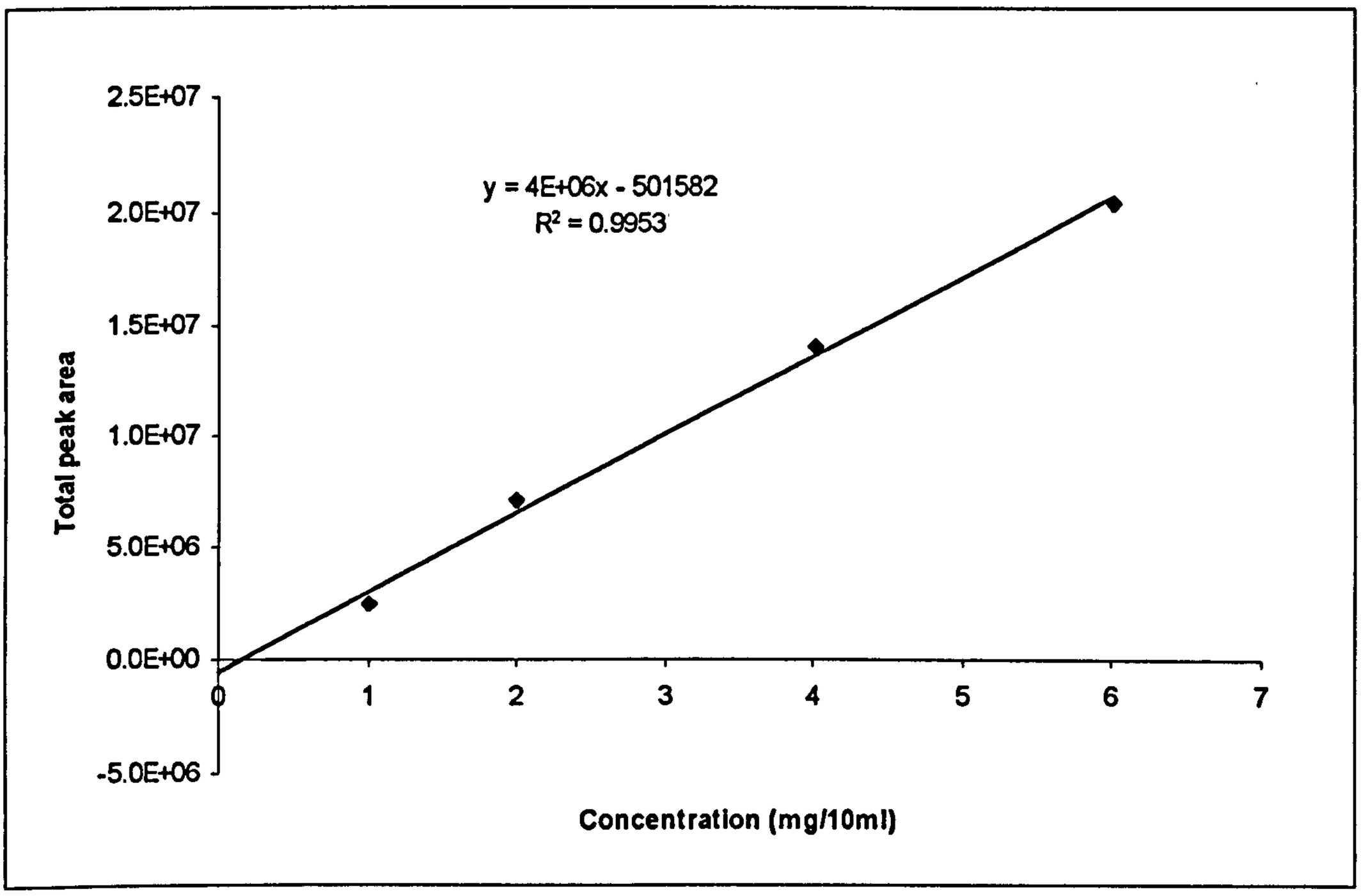
Figure 4.32: HPLC chromatogram of 1 mg Voranol P400 derivatised with phenyl isocyanate and diluted in 10 cm^3 acetonitrile.



The HPLC detected a number of peaks up to two minutes which were believed to be reaction products of the phenyl isocyanate, i.e. as urea and biuret etc. This is deduced by comparison with an chromatograph of phenyl isocyanate after heating for 3 hours at 90°C. Hence the total peak areas of interest all occur after two minutes.

After gaining an understanding of the peaks in the HPLC chromatogram a number of Voranol P400 standards were prepared and derivatised for analysis by HPLC, the total peaks areas of the resulting chromatograms after two minutes were plotted into a calibration curve (Figure 4.33) before derivatisation and analysis of the residues from the commercial laminate samples.

Figure 4.33: Calibration curve of Voranol P400 standards derivatised with phenyl isocyanate and diluted in 10 cm^3 acetonitrile.



The equation of this calibration curve was used to determine the polyol migration of a number of commercial laminate pouches into water and the degree of migration of 1 g of Voranol P400 through a 45 mm polyethylene film into water (see sections 4.2.4.3 and 4.3.1.3). The commercial laminates containing this difunctional polypropylene glycol were samples 2, JSD and 484.

The derivatised residues were injected onto the HPLC column several times and the average peak area was calculated and incorporated into the calibration equation to determine the amount of polyol in the migration residue. The overall migration results from chapter 2 have also been included in the table to determine the proportion of polyol species in the migration residue of the commercial laminate samples.

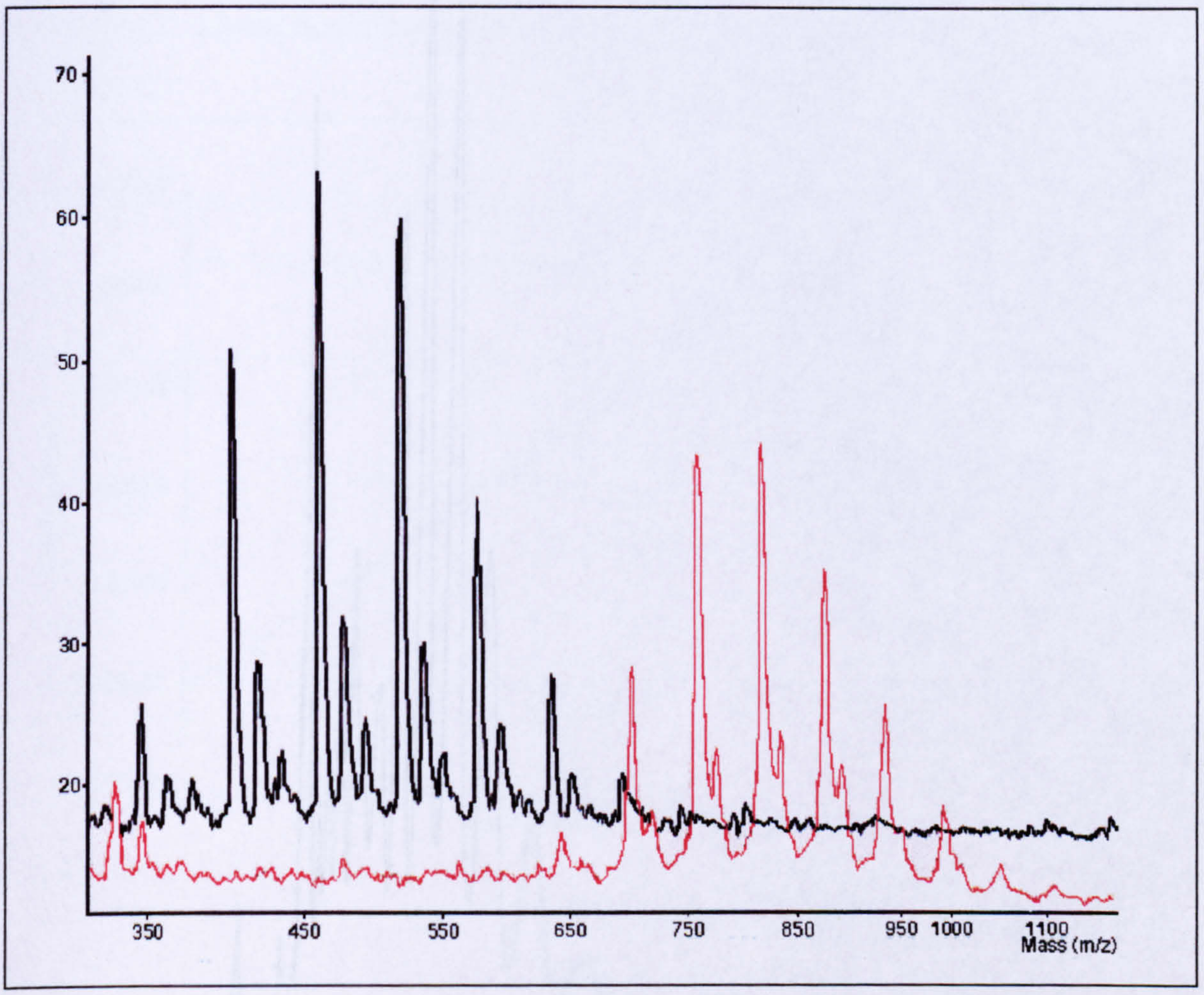
Table 4.9: Concentration of migrated difunctional polypropylene glycol in commercial laminate samples and through 45 µm polyethylene film

Sample	Total peak area	Conc (mg/10 cm^3)	Concentration	Overall migration (mg/dm^2)
1.0018g Voranol P400	23091916	5.898	5.888 mg/g	-
1.0035g Voranol P400	18038530	4.635	4.619 mg/g	-
Sample 2 -EVAP	0	0.000	0.000 mg/g	0.113
Sample 2 - SPE	0	0.000	0.000 mg/g	0.106
Sample JSD - EVAP	3188477	0.923	0.115 mg/dm^2	-
Sample JSD - SPE	1673825	0.544	0.068 mg/dm^2	-
Sample 484 - EVAP	1540915	0.511	0.064 mg/dm^2	0.100
Sample 484 - SPE	9048	0.128	0.016 mg/dm^2	0.067

The results show approximately 0.5% migration of the polyether oligomers through the polyethylene film, which if considered when looking at the migration data of the commercial laminate samples indicates a great deal of free polyether oligomers present in the polyurethane system. No derivatisation took place even with the liquid polyol sample of sample 2 and although derivatisation of the laminate pouch migrants was carried out a number of times the derivatisation reaction was unsuccessful. By comparing the results of the polyol migration with the overall migration of Sample 484 in one case the polyol accounts for 64% of the total migration residue and in the other it accounts for only 24%.

Liquid polyol sample 1 was then derivatised and analysed by MALDI-MS to check complete derivatisation and confirm the functionality of this polyether polyol sample.

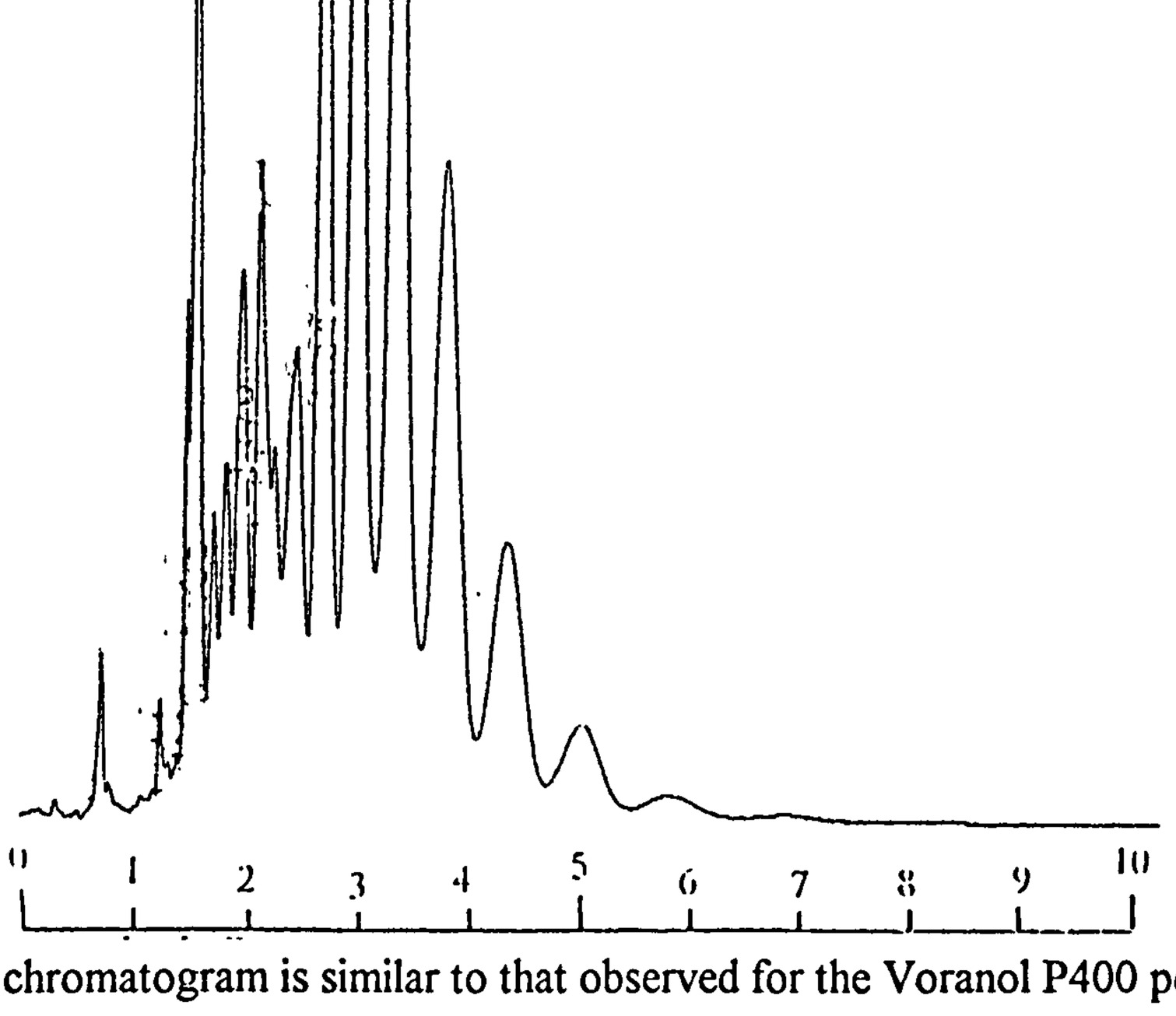
Figure 4.34: MALDI mass spectra of liquid polyol sample 1 in ethyl acetate and the sample in acetonitrile after derivatisation with phenyl isocyanate.



These spectra show both the total derivatisation (red) of the polyol and a mass shift of 360 units to the right, corresponding to 3 phenyl isocyanate molecules and hence a polyol functionality of three.

The derivatised polyol sample was then analysed by HPLC with UV detection at 240 nm. The resulting chromatogram is provided in Figure 4.35.

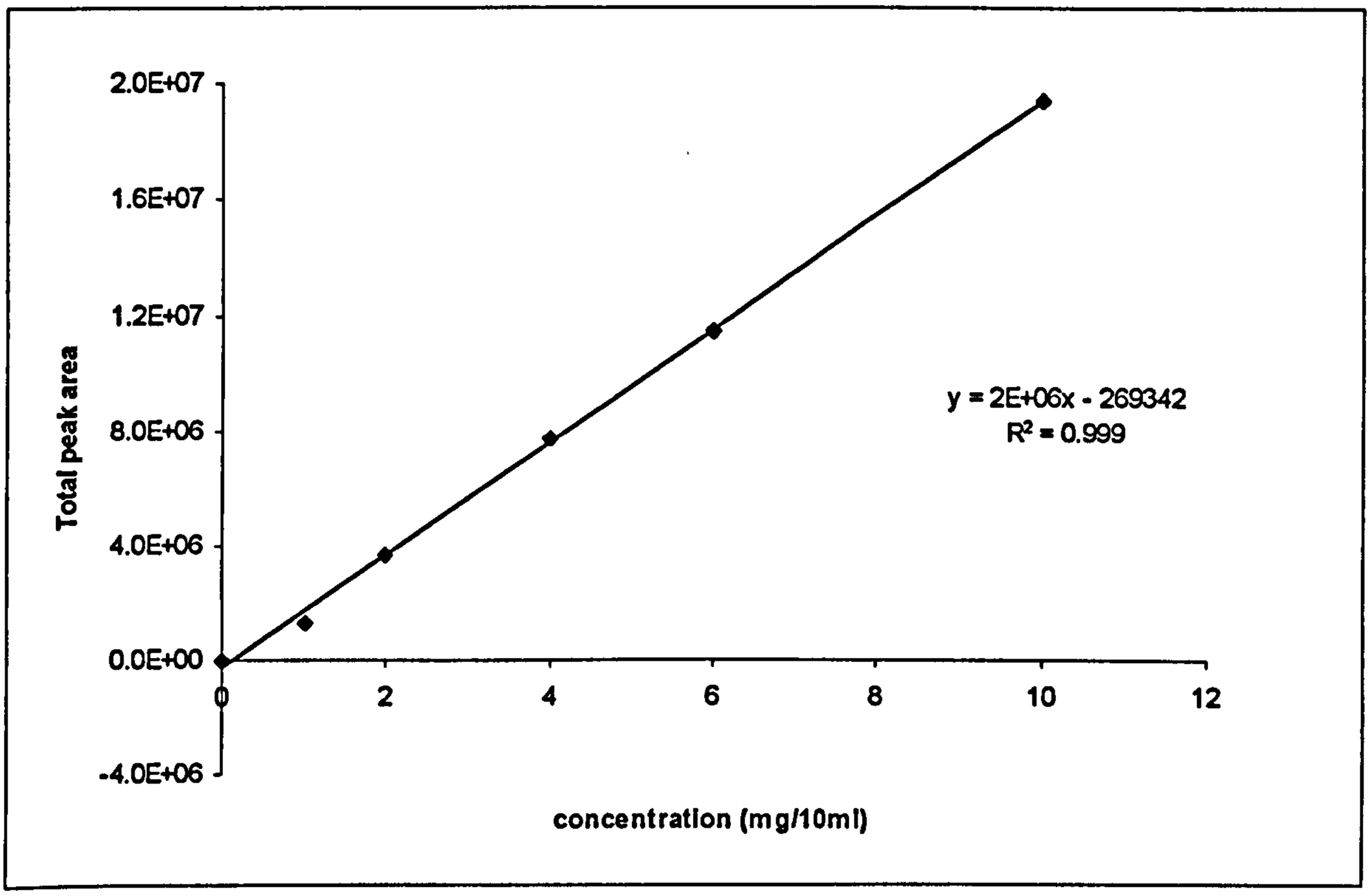
Figure 4.35: HPLC chromatogram of 1 mg liquid polyol sample 1, derivatised with phenyl isocyanate and diluted in 10 cm^3 acetonitrile.



The HPLC chromatogram is similar to that observed for the Voranol P400 polyol sample. A number of peaks at the start of the trace can be assigned to phenyl isocyanate and its derivatives (urea and biuret etc.) while the peaks detected after 2 minutes can be attributed to the reaction products of the polyether oligomers with the isocyanate.

The successful detection of these peaks led to the preparation and derivatisation of a number of known standards for analysis. The total areas, after two minutes retention time, were plotted to give a calibration curve for use as an external standard for quantifying the migrated polyol residue in pouches of commercial laminate samples.

Figure 4.36: Calibration curve of liquid polyol sample 1 standards derivatised with phenyl isocyanate and diluted in 10 cm^3 acetonitrile.



The calibration curve shows good correlation and the linear equation was then used to determine the concentration of the migrated polyol in the migrants from the commercial laminate samples and the migration residue of the 45 μm polyethylene pouch containing 1 g of liquid polyol 1 into water.

The migrated liquid polyol sample 1 through the polyethylene film (section 4.2.4.3) was derivatised together with the dry residues from the pouch extracts, into water, of samples 1, Z and 481. These derivatives were injected onto the HPLC column several times and the total peak areas of the derivatised polyols were inserted into the calibration equation and the concentrations calculated. These results can then be compared to those obtained in the overall migration studies in chapter 2 to see what proportion of the migrants are polyol species.

Table 4.10: Concentration of migrated trifunctional polypropylene glycol oligomers in commercial laminates and through polyethylene film.

Sample	Total peak area	Concentration (mg/10 cm^3)	Concentration	Overall migration (mg/dm^2)
1.0013g polyol 1	2888008	1.579	1.577 mg/g	-
1.0030g polyol 1	3113829	1.692	1.687 mg/g	-
Sample 1 - EVAP	291327	0.280	0.035 mg/dm^2	0.100
Sample 1 - SPE	204867	0.237	0.029 mg/dm^2	0.163
Sample Z- EVAP	4711	0.137	0.017 mg/dm^2	0.063
Sample Z - SPE	3070	0.136	0.017 mg/dm^2	0.037
Sample 481 - EVAP	15056	0.142	0.018 mg/dm^2	0.025
Sample 481 - SPE	32876	0.151	0.019 mg/dm^2	0.029

The migration of the trifunctional polyether through the polyethylene film appears to be 0.16% of the total oligomers available. The migration of the polyol in the commercial laminate samples suggests that between 18 and 66% of the total migrants in the pouch residue are polyol oligomers, however this result is dependent on the additives present in the polyurethane system and the polyethylene film.

4.4 DISCUSSION

The MALDI mass spectrometer proved an excellent tool for the identification of both polyether and polyester oligomers in terms of the repeat unit and the initiator or starting molecule. The gentisic acid also proved itself a good matrix for the analysis of hydroxyl terminated compounds in most cases regardless of the solvent used.

Not only did the investigations into the Voranol polypropylene glycol samples confirm the ability of the MALDI but it provided an insight into the different molar distributions that can be obtained from the same polyol. Distributions around 400, 1010 and 2000 were observed. This difference in molecular weight distribution is achieved during polymerisation by differing the molar ratio of the initiator and the alkylene oxide (in this case propylene oxide). Hence the more initiator added, the smaller the average chain length and the more initiator added in relation to the alkylene oxide, the more oligomers are produced with shorter chain lengths.

The analysis of the simple polyester polyol component provided a simple mass spectrum of evenly distributed peaks indicating the same repeat unit in each case which makes determination of the polyester relatively straight forward. However, the addition of more than one glycol or carboxylic acid molecule can complicate the resulting spectrum tremendously as this leads to the formation of a number of different polyesters. This is shown in the analysis of sample 3 which combines three reactants, one carboxylic acid and two glycols. The resulting mass spectrum showed a number of peaks distributed in a relatively random fashion.

In the production of polyesters both the carboxylic acids and the glycols are multi-functional, usually difunctional or trifunctional, and so the possibility of cyclic polyester formation is prevalent. This is the addition of the molecule from one end of the chain to the other, producing a cyclic polymer with no functional groups. During production, vacuum stripping is used to remove these unwanted oligomers. This is not very efficient as when prepared these mixtures are viscous liquids or waxy at room temperature and cannot be purified by distillation or recrystallisation. Hence in most polyester polyols, cyclic oligomers without any functional groups will be present and without any functional groups no reaction with the isocyanate group will take place. Therefore the cyclic polyesters will remain as low molecular weight oligomers free to migrate. This is shown in the results of two polyester systems TC1 and sample 3. No peaks corresponding to cyclic oligomers from samples 4 and 5 were detected. The glycol used in samples 4 and 5 was neopentyl glycol which due to steric hindrance will not favour the formation of cyclic species, or it may just be that after the production of this polyester, the vacuum stripping was more successful and any level of cyclic migration to too low for detection.

The migration of cyclic polyesters is not unexpected as they lack any functionality for the reaction with the isocyanate groups. However migration of polyether oligomers is noted even though they contain a functional hydroxyl groups for reaction with the isocyanate component. In the laboratory cured systems the presence of these functional oligomers suggested a lack of isocyanate in the initial reaction mixture. The components were added in a 1 : 1 ratio as the correct formulation was unknown.

The migration through the polyethylene film pouch of the polyol component illustrates the ability of both polyether and polyester oligomers to migrate through an average thickness of polyethylene film with little restriction in most cases. However, the extent of migration is dependent on the structure of the polyol in question. This is shown by comparing the migration of the difunctional and trifunctional polyether samples; the difunctional polyether migrates with little restriction up to 1,600 mass units whereas the polyethylene

film acts as a barrier for the trifunctional polyethers beyond 575 mass units. This is due to the differences in the structure of the polyethers. The difunctional polymer will contain a long chain linear polypropylene glycol with hydroxyl groups at each end and the trifunctional polyether is a branched polymer with three hydroxyl groups at the end of three polypropylene oxide chains.

The MALDI analysis of the commercial laminate samples detected the migration of polyether oligomers. As mentioned, this was totally unexpected especially when considering that during lamination the polyurethane system is mixed containing excess isocyanate to facilitate ease of handling which should completely react with all of the available hydroxyl groups during curing, leaving none to migrate. Three possible reasons for this are suggested: The excess isocyanate may react with atmospheric moisture as this is a more favourable reaction than with the secondary hydroxyl groups of the polyethers. Although, when the isocyanate does react with atmospheric moisture to produce the amine which will react again with another isocyanate group to produce a urea and biuret. These derivatives cause the final laminate to bubble which is known in the industry as the anti-seal effect. Another possible reason for a lack of polyether reaction is the migration of the polyether oligomers into the polyethylene film where it resides in a kind of reservoir away from the polyurethane system and thus unable to react with the isocyanate species. Another explanation may be the reaction of the polyether oligomers with an acid stabilizer used to control the reaction. This may produce a kind of polyether salt unable to react with the isocyanate group, which during migration is hydrolysed back to the hydroxyl terminated polyether. By this time the isocyanate groups have fully reacted and so the polyethers migrate unreacted.

Migration is noted with the functional polyether oligomers but none of the functional polyester species were detected. This suggests that either the polyester isocyanate reaction is very favourable and goes to completion or the polyester oligomers do not migrate into the polyethylene film and remain in the polyurethane system for complete reaction with the excess isocyanate groups.

The MALDI-MS detected the presence of cyclic oligomers from the commercial laminate pouches that had previously been identified in the cured adhesive extracts. This demonstrates the ability of the cyclic species to migrate through the polyethylene film even though they are relatively bulky.

Quantification of these cyclic species has proved unfruitful with the analytical equipment available. A lack of a chromophore in all cases has dismissed the use of UV detection and the lack of a functional group has made simple derivatisation impossible.

The presence of the functional groups in the polyether migrants led to the successful derivatisation of the oligomers with phenyl isocyanate to produce a good chromophore for UV detection. In the derivatisation of these species the MALDI was used to confirm complete derivatisation and the functionality of the polyether. The results show that migration of the difunctional polyether is greater than that of the trifunctional polyether, in the case of the former 0.5% of the free oligomers migrated compared to 0.16% in the case of the latter. This was also reflected in the results of the pouch laminate migrants. For difunctional polyethers the level of migration was between 0.016 and 0.115 mg/dm^2 and in the case of the trifunctional polyether laminates between 0.017 and 0.035 mg/dm^2, which although the lower levels are comparable the higher levels are very different. This degree of difference in the levels of migration is again due to the structure of the oligomers and selectivity of the polyethylene film, with the difunctional species being linear and the trifunctional being branched and bulkier.

CHAPTER 5

ANALYSIS OF THE ADDITIVE MIGRANTS

5.1 INTRODUCTION

In addition to polyfunctional isocyanates and polyols a wide range of auxiliary chemicals may be used to control and modify both the polyurethane reaction and the properties of the final polymer. In the case of polyurethane adhesives these additives include catalysts, branching agents, antioxidants and reaction stabilisers.

The main types of catalyst used in polyurethane formation are tertiary amines and organometallic compounds, especially tin compounds. The mechanism of catalysis by a tertiary amine involves the donation of electrons by the tertiary nitrogen to the carbonyl carbon of the isocyanate group thus forming a complex intermediate. The catalytic activity of a tertiary amine depends on its structure and basicity. The catalytic effect increases with increasing basicity but is reduced by steric hindrance of the aminic nitrogen. Organometallic catalysts form an intermediate complex with the isocyanate group and the hydroxyl group of the polyol.

Branching agents are low molecular weight polyols or polyamines with functionality of three or more. They are used to increase the bonds between longer chain oligomers in polyurethane systems.

Many antioxidants used in polyurethanes can also be used in a number of other polymers, which indicates that they operate by interfering with the agents of photo-oxidation rather than by a specific interaction with the particular polymer. One general mechanism by which antioxidants act is by reaction with peroxy radicals. In doing so they compete with the polymer, thus reducing the extent to which the degradation mediated by peroxy radicals can occur.

Reaction stabilisers are used to control the reaction rate. They are usually acidic compounds present in the polyol component, their presence in the polyurethane reaction mixture results in acidic conditions. This reduction in reaction pH accelerates the reaction and thus polyurethane formation.

A great deal of work has been published on the analysis of additives in and migrating from food packaging materials, the majority of which are concerned with additives from plastics like polyethylene and polypropylene. However a number of additives are common in both plastic films and polyurethanes and so certain methods can be applied to both types of polymer.

A wide range of analytical techniques are utilised for the analysis of additives. These include on line methods for the extraction, separation and identification of monomers, additives and oligomers in a single step. One such method is cited generally for the separation of polymers and incorporates a special guard column and multi solvent gradient liquid chromatography with UV detection, although specific identifications are limited[68].

An on line extraction, separation and identification method for the analysis of biocompatable polyurethanes for additives is presented using supercritical fluid extraction - supercritical fluid chromatography - mass spectrometry[69]. In every polyurethane this method was applied to both antioxidants and plasticizers where identified, although the polyurethanes looked at were not adhesives but for use as implants in living tissue. A comprehensive method for looking at a number of additives in polyolefins is presented by Haney and Dark[70] including the antioxidants Irganox 1076 and 1010 and BHT. Analysis was carried out using reversed phase high performance liquid chromatography with simultaneous UV and refractive index detection. A high performance size exclusion chromatography method has also been developed for the analysis of additives, their degradation products and any other low molecular weight compounds present in plastics[71].

Surface analysis has shown the presence of additives on the surface of polymers. The movement of these additives is possible as they are relatively free of spectral interferences due to the polymer matrix. One cited method of surface analysis is time of flight static secondary ion mass spectrometry (TOF SSIMS) for the identification of additives on the surface of polyethylene film[72]. In the analysis of additive migration in commercial laminate materials both GC-MS and HPLC have proved their worth[39], GC-MS was used to detect BHT and the antioxidant residue while HPLC detected Irganox 1010.

Because additives are often used in a number of polymer applications, it is conceivable that they may occur in both the plastic film and the polyurethane adhesive itself. Hence it seemed sensible to initially analyse the polyurethane component extracts for the presence of additives followed by the analysis of pouch laminate extracts for any additive migration from the polyurethane adhesive. GC-MS was the chosen method of analysis as it could be used for identification unlike HPLC with UV detection.

5.2 EXPERIMENTAL

5.2.1 Reagents

Millipore water (18MΩ)

HPLC grade Dichloromethane

1M Hydrochloric acid, 1M Sodium hydroxide

(Fisher Scientific, Loughborough, Leicestershire, UK)

Fluorononane

(Sigma-Aldrich, Gillingham, Dorset, UK)

5.2.2 Apparatus

Carlo Erba GC 8000 - Fisons MD 800 MS

Hulme Martin heat sealer - Dual electronic

(Hulme Martin Ltd, London, UK)

5.2.3 Samples

GC-MS studies were carried out on the following commercial laminate samples:-

Table 5.1: Commercial laminate sample extracts analysed for the presence of additives by GC-MS

Code	Configuration	Polyurethane
Sample 1	60 μm LDPE / PU / 12 μm PET	2.4 g/m^2 Polyether
Sample 2	75 μm LLDPE / PU / 12 μm MET PET (2g/m^2 PVDC)	2.5 g/m^2 Polyether
Sample 3	45 μm (75:25 LDPE:BLLDPE) / PU / 12 μm PET	1 - 1.5 g/m^2 Polyester
Sample 4	50 μm LDPE / PU / 7 μm ALU / PET	1.5 g/m^2 Polyester

5.2.4 GC-MS analysis of volatile migrants

GC conditions : Column - Silicone SE 54 (0.25μ film) capillary
: Carrier gas - Helium 1cm^3/min
: Oven prog - 40°C for 3 mins, to 280°C at 8°C/min
Hold at 280°C for 3 minutes.
: Injector temp- 300°C

1 cm^3 of the wet adhesive components and mixtures were cured on aluminium foil and extracted in 100 cm^3 aqueous food simulants by refluxing for one hour. 20 x 20 cm laminate/film pouches were sealed using a Hulme Martin heat sealer. Each pouch contained 100 cm^3 simulant and was heated for two hours at 70°C.

The aqueous simulants in each case were decanted off from the residue film, 1 cm^3 0.2M hydrochloric acid was added. The simulant was then extracted with two 25 cm^3 aliquots of dichloromethane. This was then made basic by the addition of 1.5 cm^3 0.2M sodium hydroxide, which was again extracted with two 25 cm^3 aliquots of dichloromethane. These aliquots were pooled and concentrated down to 1 cm^3 for analysis by GC-MS. Fluorononane was used as the internal standard, 50 µl of a 1 mg/cm^3 solution in dichloromethane was added to the 1 cm^3 sample. 1 µl of the samples plus internal standards were then injected onto the capillary GC column and analysed by mass spectroscopy.

5.3 RESULTS

The GC-MS analysis produced a number of peaks however using the N.I.S.T library data system comprehensive identification was limited.

In general the migratable substances are observed in all three aqueous food simulants, albeit at different levels. Hence only results of water extracts are shown as no quantitative data was available.

During the manufacture of polyurethane adhesives any additives are introduced via the polyol component. Hence even though GC analysis was carried out on all of the polyurethane components, the inner film (polyethylene) and the final laminate material the Figures given are the chromatograms for the polyol and laminate extracts of the corresponding samples. However the Tables provide information on the retention times of the peaks detected in the final laminate residue and whether these peaks were also detected in the separate polyol and isocyanate components together with the cured adhesive system. The most abundant mass spectra ions are also provided with each retention time peak of the pouch laminate material in the software of the spectrometer, together with its closest chemical match provided by the N.I.S.T library.

Figure 5.1: GC-MS chromatogram of the migrants from pouched sample 1 into water

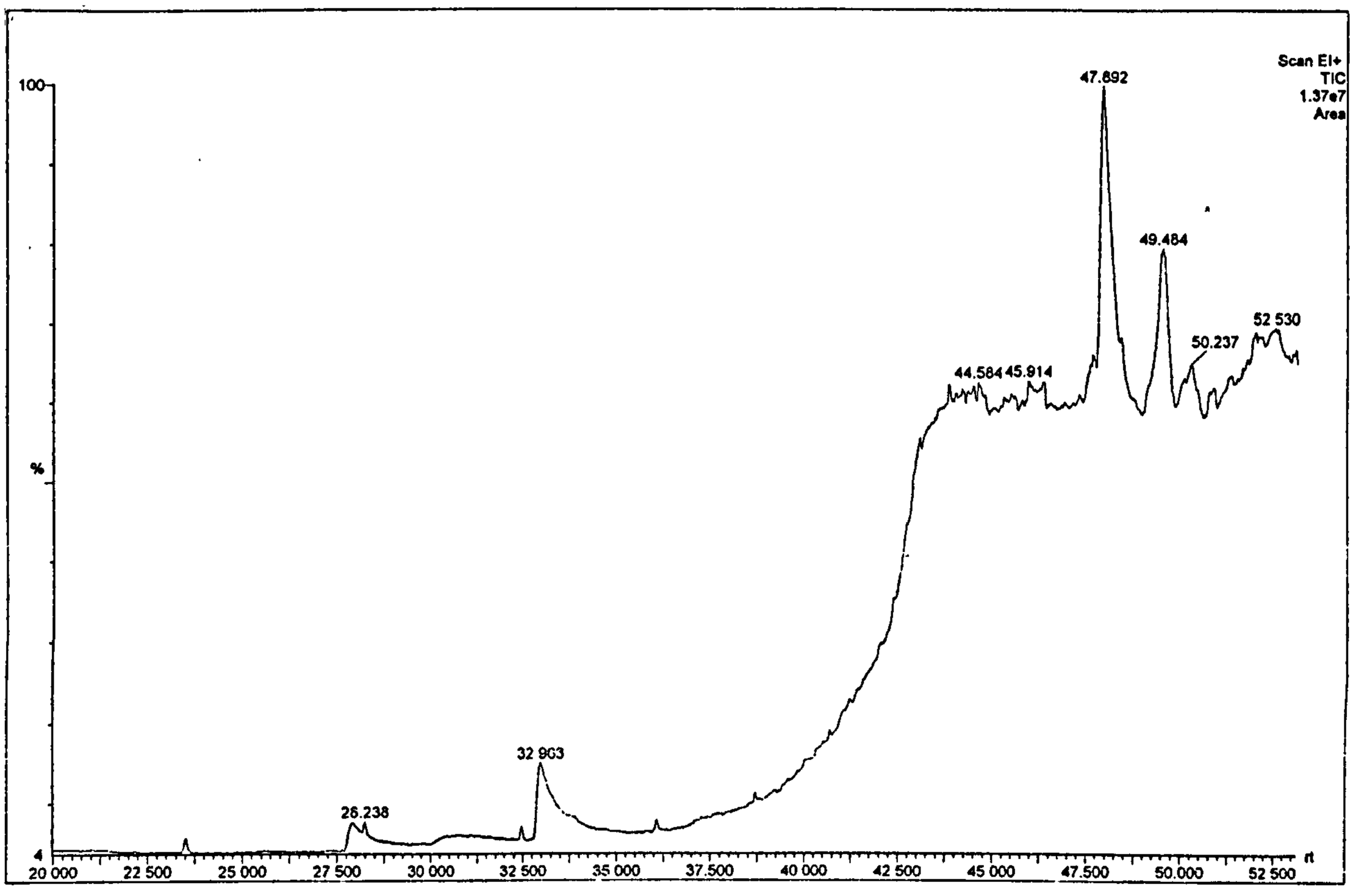


Figure 5.2: GC-MS chromatogram of liquid polyol sample 1 extracted into water

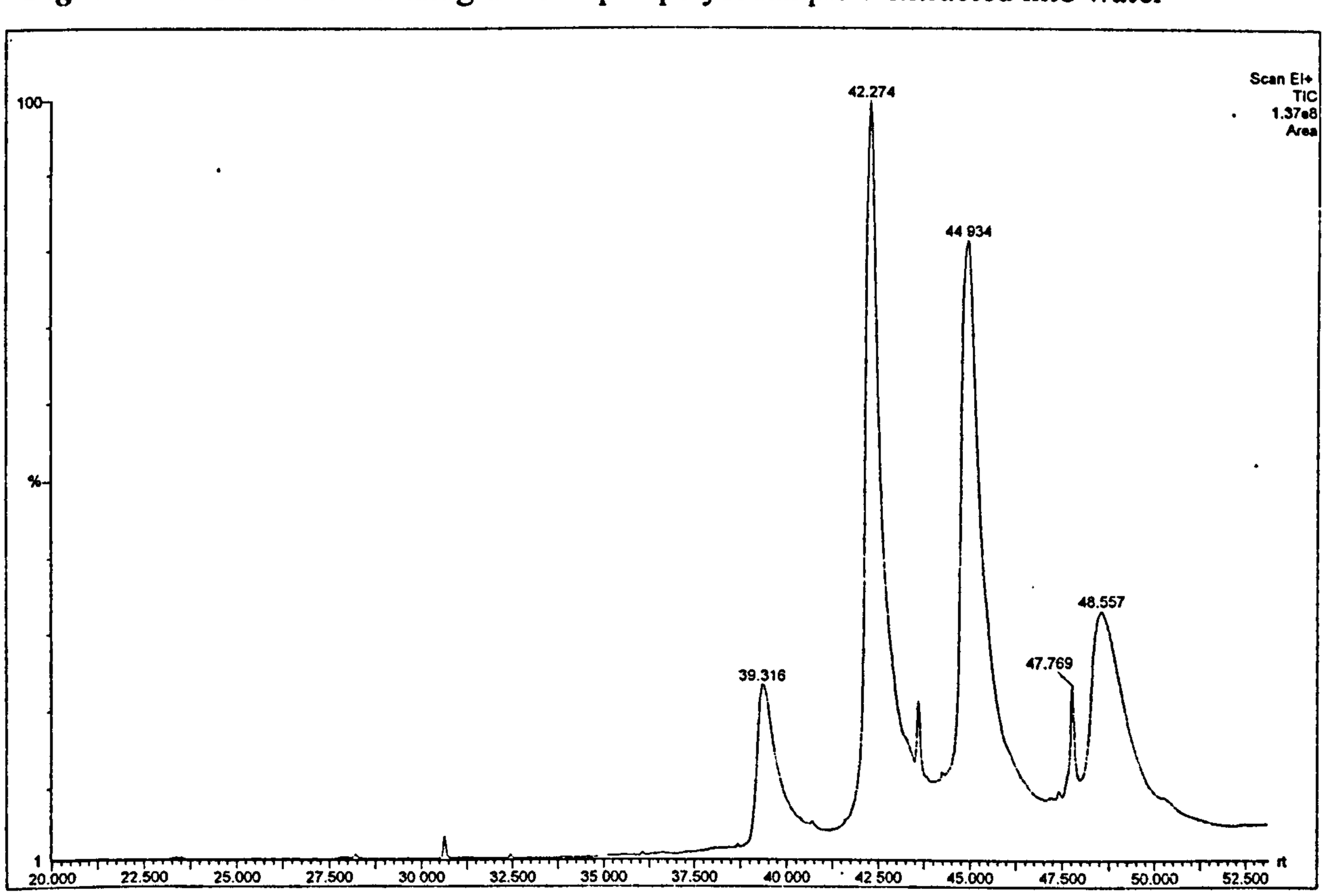


Table 5.2: Volatile migrants from pouch sample 1 by GC-MS analysis

	Retention time (mins)					
	28	**33**	**39**	**48**	**49**	**52**
Pouch	✓	✓	✓	✓	✓	✓
Polyol			✓	✓	✓	
Isocyanate	✓	✓				✓
Cured	✓		✓	✓		✓

Table 5.3: GC mass spectra ions and possible compounds of volatile migrants from sample 1

Retention time	MS Ions	Possible compound
28	59	Substituted propanol
33	59	Substituted propanol
39	31, 43, 55, 207	Octadecenal
48	207, 282, 73, 69	Glycerol trimethylsilyl ether
49	59, 117, 207, 282	Ether
52	207, 282, 73, 361	Glycerol trimethylsilyl ether

The peaks noted in the gas chromatogram of the migrants from pouch laminate sample 1 in all but two cases correspond to peaks detected in the GC of the liquid polyol sample. The mass spectrum of the peak after 33 minutes shows a peak at 59 units possibly a propylene oxide fragment or a propanol branching molecule. The peaks between 48 and 52 minutes are attributed to a glycerol trimethylsilyl ether by the N.I.S.T library, silanes are often used as additives to enhance chemical resistance in the final polymer.

Figure 5.3: GC-MS chromatogram of the migrants from pouched sample 2 into water

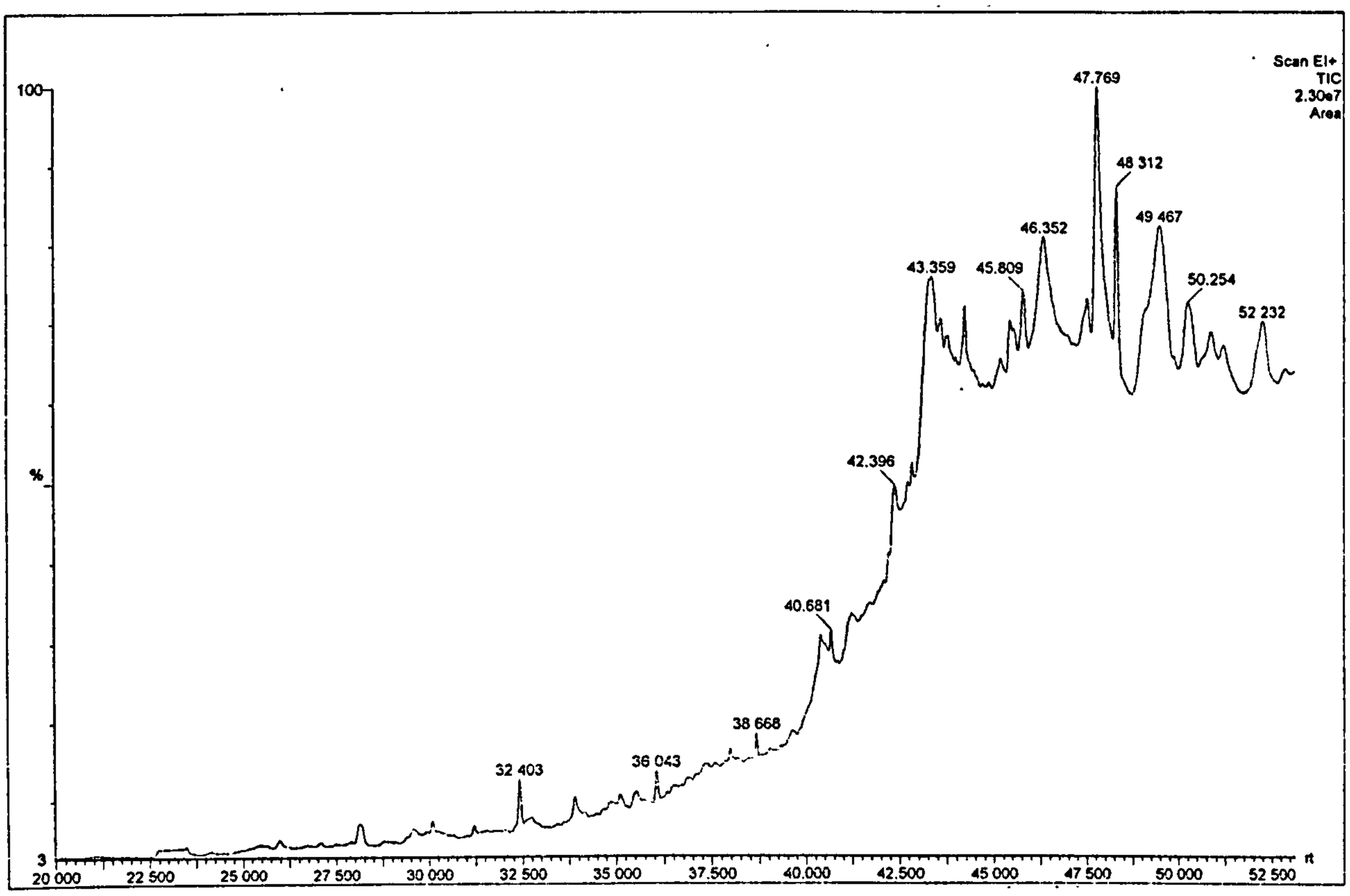


Figure 5.4: GC-MS chromatogram of liquid polyol sample 2 extracted into water

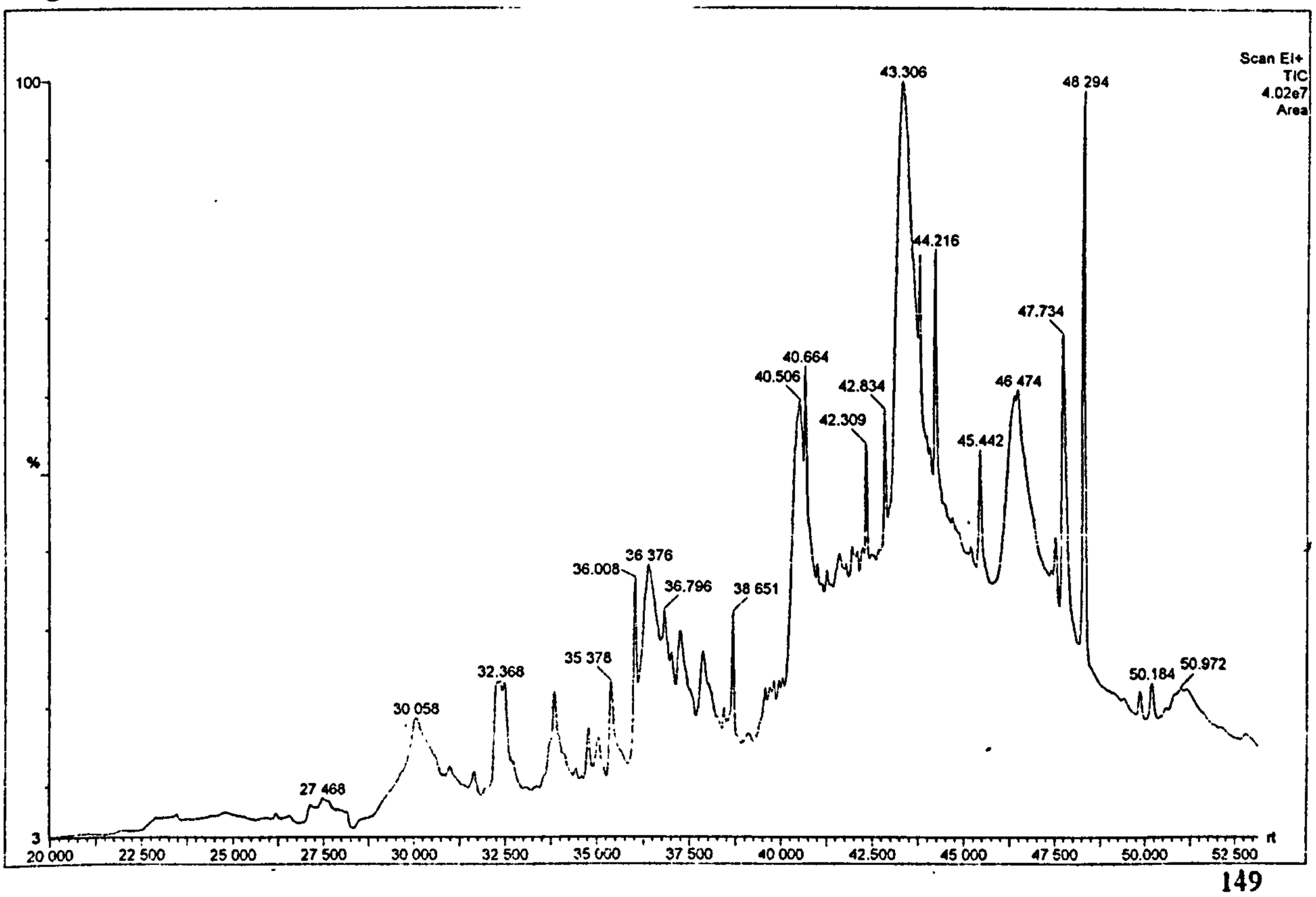


Table 5.4: Volatile migrants from pouch sample 2 by GC-MS analysis

	Retention times (mins)							
	32	**36**	**38**	**40**	**43**	**46**	**48**	**49**
Pouch	✓	✓	✓	✓	✓	✓	✓	✓
Polyol	✓	✓	✓	✓	✓	✓	✓	
Isocyanate		✓		✓				
cured	✓	✓	✓	✓	✓	✓	✓	

Table 5.5: GC mass spectra ions and possible compounds of migrants from sample 2

Retention time (mins)	MS Ions	Possible compound
32	31, 73, 361, 147, 221	Siloxane
36	31, 43, 59	Decanol
38	31, 73, 43, 41, 59, 282	Hexanol
40	59, 207, 31, 41	Branched pentanol
43	59, 207, 117, 282, 41	Branched decanol
46	207, 59, 282, 73, 117	Siloxane
48	207, 282, 215, 59	Siloxane
49	207, 282, 69, 55	Siloxane

All but one GC peak from the pouch migrants from sample 2 are also observed in the GC of the liquid polyol sample. The first peak after 32 minutes corresponds to a siloxane as do those between 46 and 49 minutes. These may be additives used to enhance chemical resistance or fragments of the packing from the GC capillary column. All of the other peaks were identified as branched alcohols, possible polyol fragments or branching agents added to the polyurethane system to promote non linear expansion.

Figure 5.5: GC-MS chromatogram of the migrants from pouched sample 3 into water

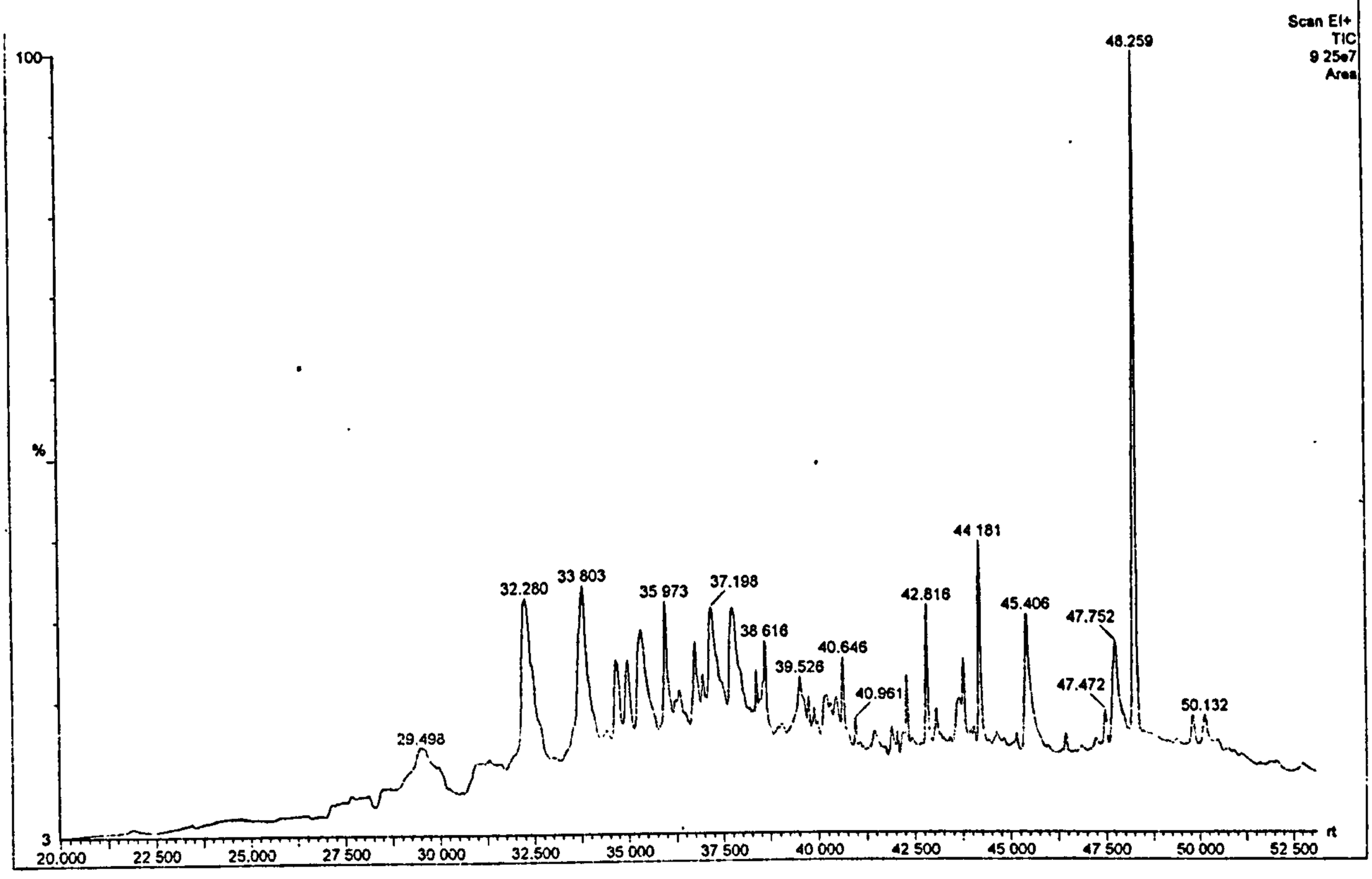


Figure 5.6: GC-MS chromatogram of liquid polyol sample 3 extracted into water

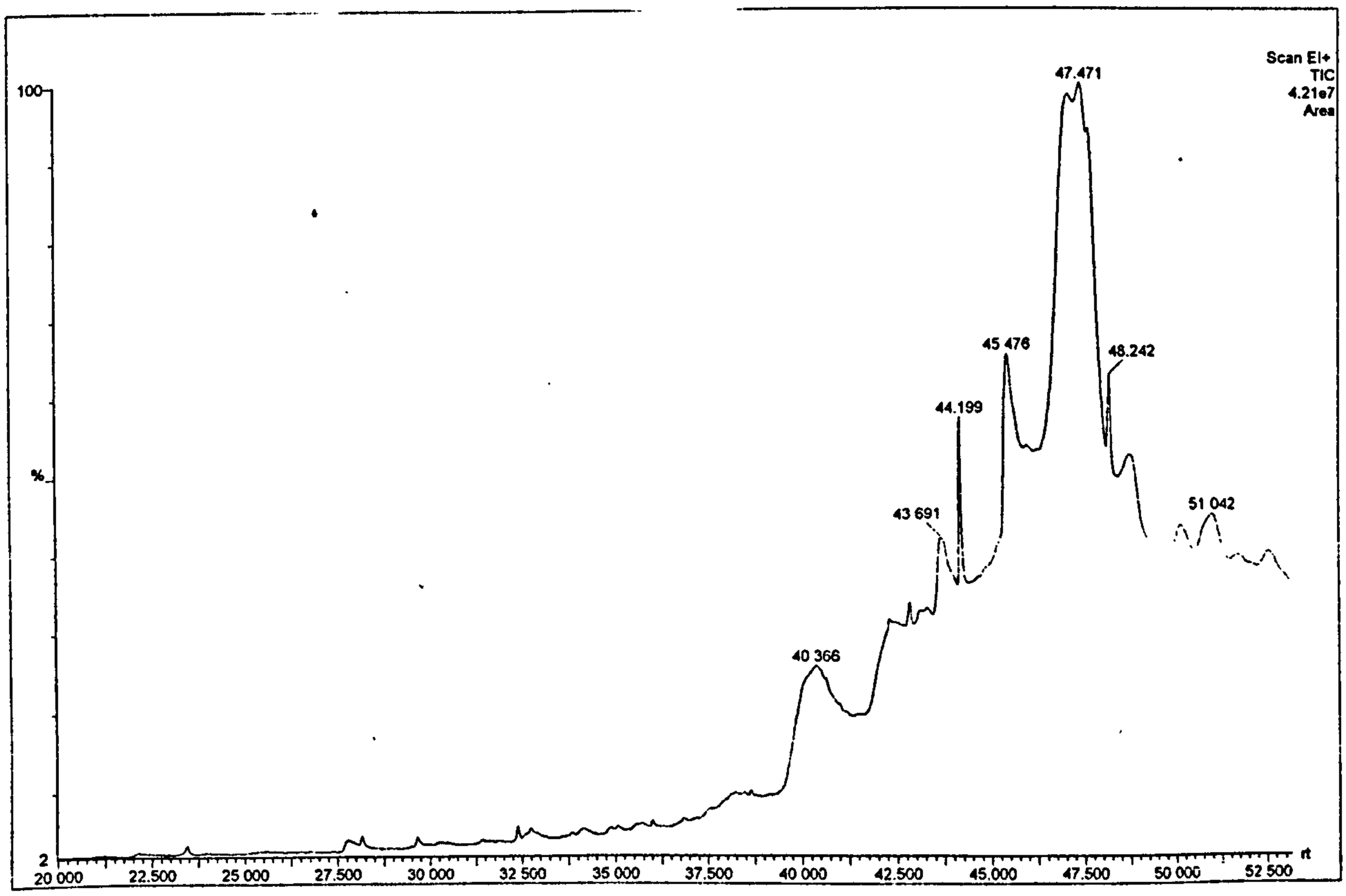


Table 5.6: Volatile migrants from pouch sample 3 by GC-MS analysis

	Retention times (mins)								
	32	**34**	**36**	**37**	**41**	**43**	**44**	**45**	**48**
Pouch	✓	✓	✓	✓	✓	✓	✓	✓	✓
Polyol	✓	✓	✓	✓	✓	✓	✓	✓	✓
Isocyanate			✓						
Cured	✓			✓	✓	✓	✓		

Table 5.7: GC mass spectra ions and possible compounds of volatile migrants from sample 3 into water

Retention times	**MS Ions**	**Possible compounds**
32	55, 69, 83, 97, 111, 238	Pentadecene - 95% match
34	55, 69, 83, 97, 111, 252	Octadecene - 99% match
36	73, 60, 120, 256, 213	Hexadecanoic acid
37	55, 60, 83, 97, 264	Octadecenoic acid
41	55, 43, 41, 173, 207	Branched undecanol
43	173, 99, 55, 113, 217	Diethyl hexyl phthalate
44	149, 167, 57	Carboxylic acid
45	173, 207, 55, 73, 282	Decanoate
48	69, 81, 41, 67	Squalene

The first two peaks detected by the GC in the analysis of the pouch migrants are a 95% match for the alkenes pentadecene and octadecene. The next two peaks match to the mass spectra of carboxylic acids and are probably artefacts of the polyester species, as too is the peak after 44 minutes.

Figure 5.7: GC-MS chromatogram of the migrants from pouched sample 4 into water

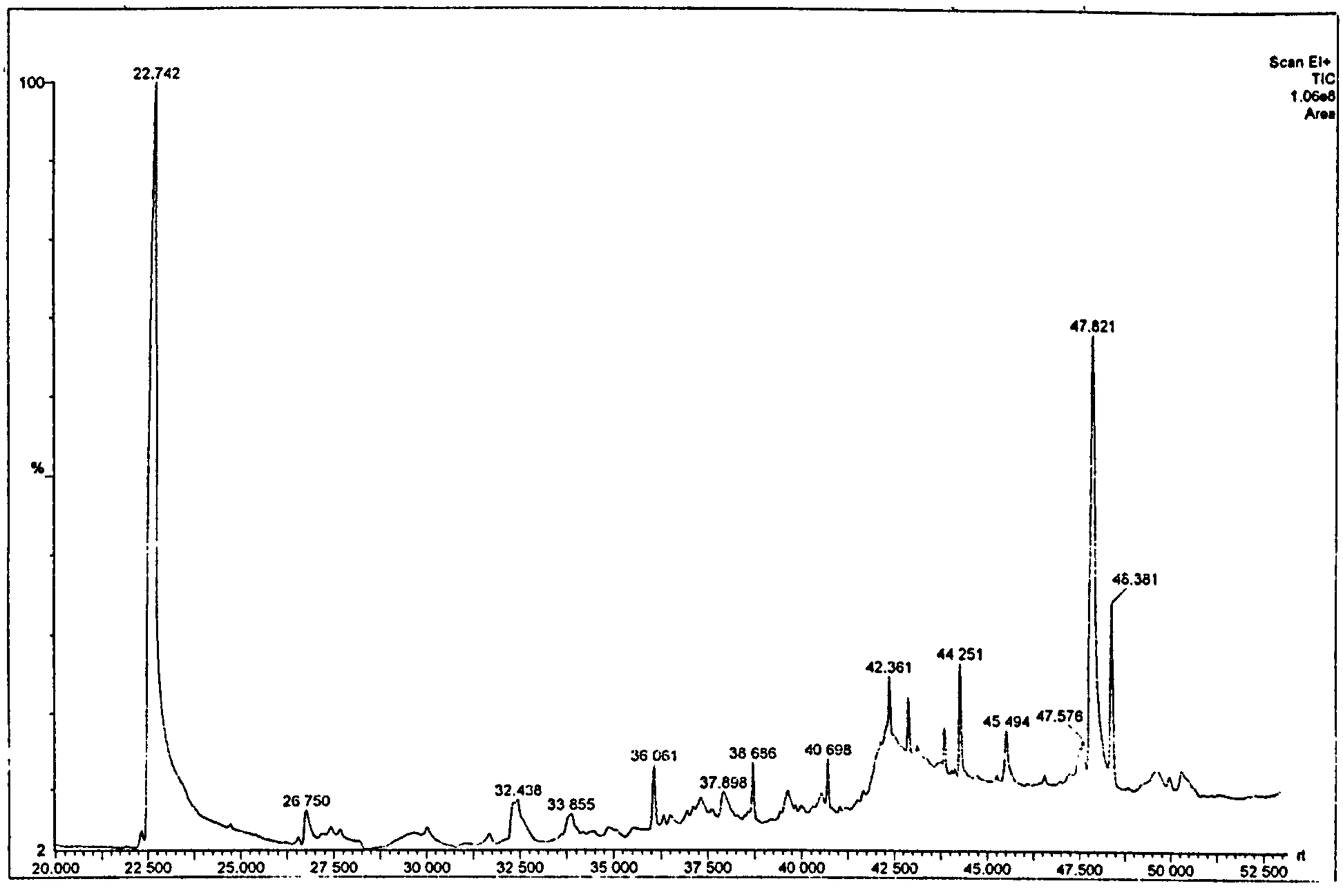


Figure 5.8: GC-MS chromatogram of liquid polyol sample 4 extracted into water

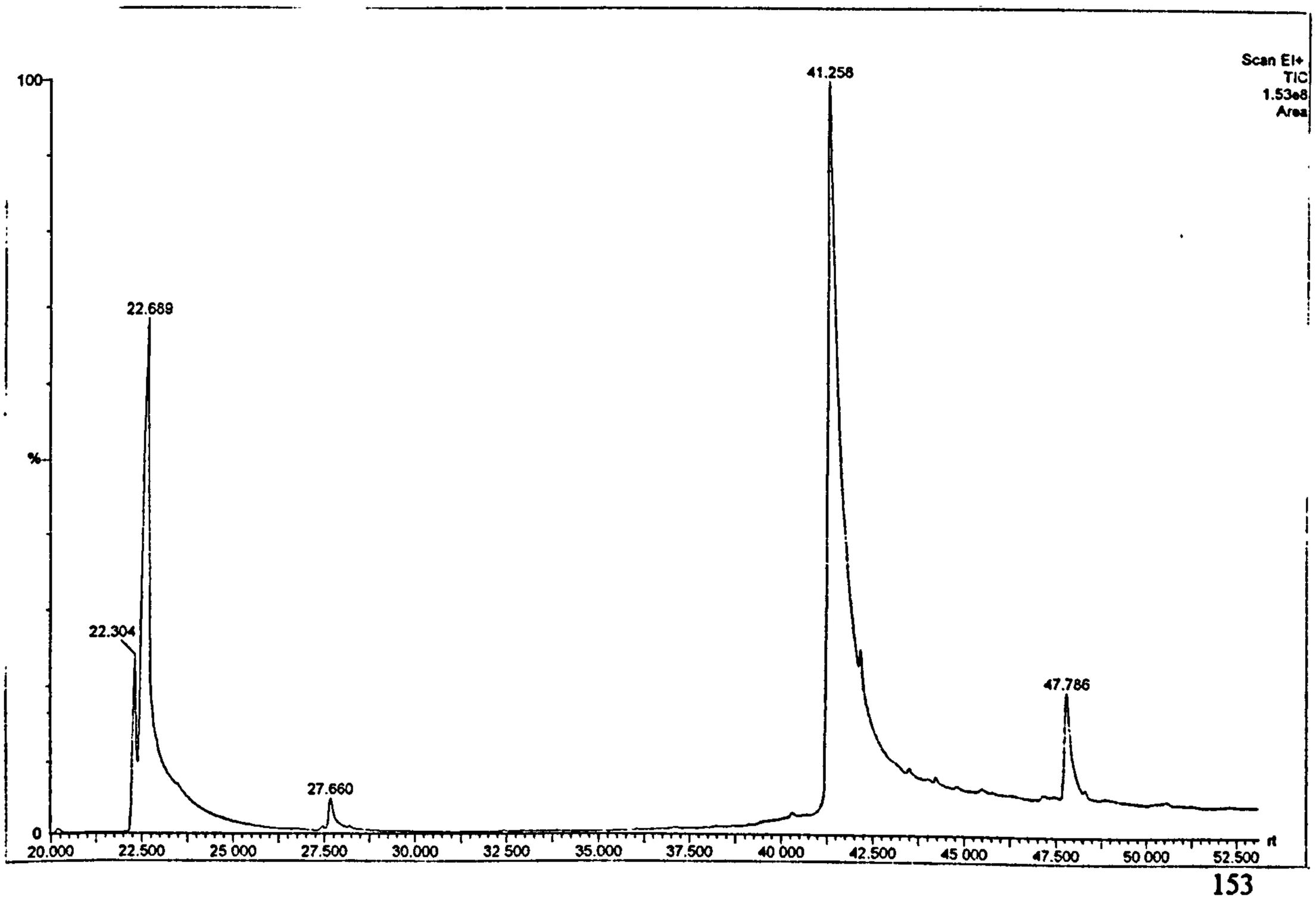


Table 5.8: Volatile migrants from pouch samples 4 and 5 by GC-MS analysis

	Retention times (mins)								
	23	**27**	**32**	**36**	**39**	**41**	**42**	**44**	**48**
Pouch	✓	✓	✓	✓	✓	✓	✓	✓	✓
Polyol	✓	✓			✓	✓		✓	✓
Isocyanate				✓					
Cured	✓	✓		✓	✓	✓		✓	✓

Table 5.9: GC mass spectra ions and possible compounds of migrants from samples 4 into water

Retention time	MS ions	Possible compound
23	43, 103, 145	Triacetin
27	55, 111, 129, 41	Hexanedioic acid, ester
32	73, 43, 32, 361	Hexadecanol
36	73, 444, 147, 221	Siloxane
39	73, 282, 147, 32	Glycerol ether
41	129, 55, 111, 215	Hexanedioic acid ester
42	129, 73, 55, 207	Octadecanoic acid, ester
44	149, 207, 167, 57	Carboxylic acid
48	207, 215, 282, 55	Undecanol

The first peak after 23 minutes is identified as triacetin, an additive used to promote branching within polyurethane systems. The peaks after - 27, 41, 42 and 44 minutes have all been identified as carboxylic acid esters which of course the polyol component is. A glycerol ether is observed after 39 minutes and this is possibly an artefact of the branching agent. Two alcohols are noted after 32 and 48 minutes and another siloxane after 36 minutes.

5.4 DISCUSSION

The GC-MS analyses detected a number of compound groups migrating from both the liquid polyol component and the commercial laminate pouch. The absence of any exact identification may be due to:

The absence of the particular compound from the NIST data-base
The use of impure commercial materials
The lack of a significant molecular ion peak.

Many commercial materials used in the polymer industry are described as the reaction products of ....., and are therefore not adequately categorised to be in the NIST data-base. Oligomeric material likewise is unlikely to be included in the data-base.

Electron impact ionisation produces mass spectra with much fragmentation data and often little molecular ion information. Chemical ionisation offers a a milder method of forming ions and so is more likely to provide information on relative molecular masses. MALDI presents the converse of this situation ie there is no fragmentation and thus the only information available is the molecular ion.

One way to overcome this lack of exact identification is to compile an in-house library of additive mass spectra for comparison with mass spectral data from the migrating species. Bonell and Lawson[12] prepared a list of compounds used in adhesives for food packaging, this provides a list of possible additives which could be obtained and run on a GC-MS for future comparison. One disadvantage of this approach is that the analysis of pure additives will not provide any information on the potential degradation products of the additives that might be migrating from the adhesives.

The GC-MS analysis of the migrants from the pouched laminate material provided complex chromatograms with clusters of small peaks which in a number of cases represent the same type of compound i.e. the same m/z values are present for each peak. These chromatograms include migrants from both the plastic film (inner layer) and the polyurethane adhesive plus possible migrants from the outer film. To determine which migrants in the laminate samples were from the adhesive layer, analyses were also performed on cured mixed adhesives which were prepared in the laboratory at a 1:1 ratio polyol: diisocyanate. This may not quite represent industrial practice since the industrial mixing uses sophisticated equipment to thoroughly mix exact proportions of each component under specified conditions.

The main type of additive from the adhesive layer were cross linking and chain extending agents from the polyol component. These are alcohols with a functionality of 3 or more, for example triacetin. Siloxanes were identified in samples 2 and 4, these are added to increase chemical resistance in the final polyurethane system.

The GC-MS also detected polyol oligomers in the pouch migrants including ethers, carboxylic acids and esters. This confirms the results obtained by the MALDI-MS (in Chapter 4) of the laminate migrants. One peak common to more than one adhesive is a carboxylic acid peak at 44 minutes in samples 3 and 4, which both contain adipic acid.

GC-MS is the only method used which specifically detected additive migrants but it will only monitor species which are volatile within the GC-MS apparatus. The presence of catalysts in the adhesives are expected, these are not detected by the GC-MS as in most cases they are non-volatile under the analytical conditions. Hence another analytical technique should be employed to identify these compounds, for example LC-MS.

CHAPTER 6

CONCLUSIONS AND FURTHER WORK

Polyurethane adhesives are found in a large number of flexible food packages and used in a wide range of applications all with different requirements. Although polyurethanes are not used in direct contact with the foodstuff the polyethylene film is not a complete barrier to migration into the food. Migration of all the components in the adhesive into food simulants has been demonstrated. Migration of the diisocyanate component is well documented due to its toxicological effects and this is reflected in EU packaging legislation and the FPA Code of Practice. Additive migration is also recognised and can be linked to EU legislation on plastics as the additives used in polyurethane adhesives are common to a number of other polymers including those used as packaging materials. This study has also been concerned with the migration of the polyol component of polyurethane adhesives, an area only covered in EU legislation by the overall migration limit. Significant polyol migration was not expected due to the excess of isocyanate added in the original mixture. However, a number of analytical techniques have shown the overwhelming presence of polyol species in the migration residue from commercial laminate samples

The overall migration provided a good initial overview of the migration levels in the commercial laminate samples. Two methods of sample concentration were employed to look at the efficiency of the solid phase extraction method for retaining migrants from the aqueous simulants and the ability of organic solvents to remove them from the SPE cartridges. Comparison of the SPE method with the more conventional evaporation method revealed variable results with no definate trends, although the SPE method of concentration is less time consuming it is also more costly as the cartridges are disposable.

Higher overall migration levels were observed into the fatty food simulant this is due to the increased interaction between the simulant and the contact polymer layer which in all cases for this study was polyethylene. This absorption of the simulant into the polymer swells the film and allows the movement of free oligomers and monomers into the simulant. This swelling of the packaging provides problems when using non-volatile fatty food simulants like olive oil, as the simulant is weighed before and after contact with the

packaging, the difference being migration residues. However, a certain amount of the simulant is always retained in the swelling of the packaging resulting in simulant and subsequent weight loss. This problem led to the introduction of volatile alternative fatty food simulants one of which, isooctane was used in these studies. The results obtained in the use of fatty food simulants should be kept in context, in the experimental analysis 100% fat was used, however, in real food cases there is much less fat content and very little free fat available to migrate into the packaging. Hence these results will be over estimates, to combat this the EU introduced coefficients to correct migration values, these coefficients are specified in Directive 85/572/EEC.

The overall migration tests provided a good initial analysis to show that migration does occur in commercial laminate materials. It is a relatively simple method, which does not require any specialist equipment, for industry to ensure that potential migrants are kept to a minimum. However, these results do not give any indication as to the nature of the migration residue which is required when establishing potential toxicological effects of the residue. Plus with all of the recent developments in analytical chemistry for the determination of specific migrants this method is dated and becoming more and more redundant.

The analysis of the diisocyanate component is an important aspect of migration testing due to the hazardous effects of the isocyanate group. Two methods for this analysis are extant; an HPLC method developed by CSL and adopted by CEN and a simpler colourimetric method used by industry. Both methods have good and bad points concerning the range of isocyanates detected, the latter method is often used by industry as it employs simple analytical equipment found in most development laboratories unlike HPLC with fluorescence detection used in the former method.

In the colourimetric method used by industry aniline hydrochloride is used as the calibration standard as it is less hazardous than methylene dianiline (MDA). Comparable analyses carried out at De Montfort university showed that using aniline hydrochloride, as the calibration standard in the industrial method, overestimated the levels of actual MDA present and as a result isocyanate migration was overestimated. This ensures that EU legislation is met and from a consumer point of view is reassuring. The method of analysis adopted by DMU detected higher absorbances for the aniline hydrochloride standards and thus when used would underestimate the isocyanate / amine migration level. This difference in detection levels between the methods was only noted in the case of aniline hydrochloride as the MDA calibration standards were all comparable. The primary difference in the two methods is an SPE concentration step used to concentrate the derivatised amine in the industrial method. It should be considered that this step may be in some way interfering with the level of aniline hydrochloride in the final solution, although this step did not have any effect on the MDA calibration standards also run.

The levels of diamine may also depend on the humidity during and subsequent to the lamination process. To check this a small amount of two of the commercial laminate samples were placed into a dry atmosphere over silica within hours of lamination, while portions of the same laminate were stored under normal laboratory conditions. Amine analysis of the portions 2 months after lamination revealed that amine levels were higher in the samples stored under dry conditions. This indicates that humidity has an effect on the curing of the laminate and samples kept in dry conditions take longer to cure than those exposed to atmospheric moisture. This correlates well with industry's close control of the humidity during both lamination and storage to ensure optimum curing conditions.

All the commercial laminate samples were extracted into water and 3% acetic acid for amine determinations. The aromatic amine levels were considerably higher into 3% acetic acid than into water. Possible reasons for this include;

- Bases are more readily extracted into an acid media.
- Acetic acid is more aggressive than water and is absorbed by the inner film where it allows the easy passage of the amine and isocyanate into the food simulant.
- Acetic acid provides more stable conditions for the isocyanate and amine groups preventing further reaction of the amine and isocyanate to produce urea and biuret groups which are not detected.

The amine levels in the commercial laminate samples provided different results depending on the type of adhesive used. Solvent based adhesives produced data well within the EU limit of 1 mg/kg two days after lamination, whereas all the solvent free based adhesive systems gave amine migration levels greater than the specified EU isocyanate residue limit. This is due to the initial ratio of isocyanate added to the polyol component, in the case of solvent free systems the isocyanate is added to the polyol component well in excess to maintain the adhesive in the liquid phase. The excess level of isocyanate in the solvent free system was also detected by the CEN HPLC method carried out by CSL in Norwich, who detected the presence of MDI, at levels higher than the EU residue limit 17 days after lamination.

The glycolysis method of polyurethane de-formulation provided a good method for determining the nature of the raw components used to produce the adhesive. This glycolysis method using ethanolamine was applied to the cured isocyanate components and 1 pack adhesive systems. It provided information on the pre-polymers used in the adhesive systems and the MALDI-MS proved an invaluable tool for the identity of these pre-polymers. Observation of the cured isocyanate components together with the glycolysis results suggest that the more yellow the cured component the higher the isocyanate content and the more brittle the polymer. This yellow appearance is the discolouring of the aromatic isocyanate due to oxidation of pre-existing amino groups, followed by further oxidations of amines and the formation of coloured products such as

polypseudourea ether. The isocyanate components which formed a clear polymer were flexible and the glycolysis showed these systems contained a polyol pre-polymer and thus a reduced number of free of isocyanate groups.

The MALDI-TOF-MS proved an invaluable tool for the analysis of the polyol species, this may be attributed to: a) the measurements of extremely high molecular weights with virtually no fragmentation b) the distribution, in general, of singly charged species providing easy interpretation c) where single polymers chains are resolved, MALDI-TOF enables determination of repeating units and end group compositions[73].

The MALDI detected polyol species from the cured adhesive system and the flexible laminate migration residues. The mass spectra of the polyether polyol species show greater mass distributions at higher mean masses this is a result of the polymerisation step. The detection of polyether oligomers in the migration residue was unexpected as they contain a functional group for reaction with the isocyanate component. In the case of the polyester polyols only cyclic oligomers with no functionality were detected.

In the case of sample 4 the MALDI-MS detected a peak at 316 mass units it is believed that this peak may be due to a reaction product dimer of neopentyl glycol and isobutyraldehyde, a starting material in the production of neopentyl glycol. This product has a very pungent odour at ppb levels this is undesirable and so an alternative glycol 2-methyl propanediol is used instead of neopentyl glycol although it is not as tough or as compatible in the final polyurethane system.

The derivatisation and HPLC analysis of the polyether oligomers provided a good method of quantification of the migrating polyether species. The chromatograms produced individual peaks for each of the derivatised oligomers in a gaussian distribution like those observed in the MALDI mass spectra of the polyether oligomers. One drawback of this method is the possible interference of the phenyl isocyanate reaction products with the

derivatised polyether species as they are both resolved in a relatively short space of time. Alterations to the isocratic HPLC conditions can provide a greater time interval between the phenyl isocyanate and the derivatised oligomers, however, this produces broader peaks and in most cases the final peak is too broad for quantification. One way to overcome this problem is to employ a gradient HPLC system to improve the peak resolution of the larger derivatised peaks.

Migration of the liquid polyol component through the polyethylene film provided information on the barrier properties of the film to different types of polyol. Little restriction is offered to the migration of difunctional polyether oligomers up to 1,600 mass units as these are linear, however branched trifunctional species are restricted over 550 mass units due to its bulkier structure. Polyesters are restricted by the polyethylene film with little migration after 600 mass units.

The GC-MS analysis proved a good analytical tool for the determination of low molecular weight additive groups. Alcohols, esters and ethers were observed which are used as branching agents and chain extenders in the polyurethane systems and siloxanes used to enhance chemical resistance.

An equation is set out in chapter two to encapsulate the possible migrants from a commercial laminate sample, this is as follows:-

$$O = I + P + A$$

where O = Overall migration

I = Isocyanate migration

P = Polyol migration

A = Additive migration

This study has provided quantification for the overall isocyanate and polyol migrants in polyether based systems. This method can be applied to laminate sample 1:

Overall migration = 100 μg/dm^2

Isocyanate migration = 0.26 μg/dm^2

Polyol migration = 35 μg/dm^2

Additive migration = 64.74mg/dm^2

Hence, 35% of migration is due to the polyol

0.26% of migration is due to isocyanate

64.74% of migration is due to additives or possibly migration from the outer plastic layer

European legislation has introduced a positive list of monomers and additives for use in plastics for food packaging. This list does not encapsulate raw materials in food packaging adhesives although there is a certain degree of overlap especially with additives. Hence it is foreseeable that a similar list will be compiled for adhesives used in food packaging. Together with such lists specific migration limits are specified and although this is encouraging from a consumer view point industry are concerned about the structure of this legislation. It maintains that legislation should allow more flexibility over test methods for restricted additives and monomers. Current rules often require 'specific migration limit tests on the amount of chemical migrating into particular foods'. Industry maintain these tests are costly, difficult and slow. One technical manager estimated that testing costs could run to over £100,000 per product under current rules[74].

The increased legislation regarding the recycling of waste polymers has led to the use of recycled plastics in food packaging. Because of the permeable nature of plastic materials and their possible commercial and consumer use as containers for chemicals, these recycled polymers could contain potentially toxic contaminants, such as pesticides and industrial chemicals which could migrate from the package into the foodstuff[75]. Hence recycled plastics should be used in non contact situations like foam egg cartons, grocery

bags and polypropylene fruit baskets. The usual type of recycled plastic used in food packaging applications are those of chemically treated polymers de-formulated back to the original raw materials and then re-formulated to produce virgin plastic[76], this provides a stronger polymer than in re-used systems. For reusable packages and for packages produced from recycled materials no specific regulation has been drafted. However, work has been carried out to draft a detailed protocol which contains procedures needed to develop a comprehensive package of quality assurance criteria for use by industry and regulatory authorities for ensuring the alternative quality and safety-in-use of reused plastics for food packaging[77].

To date no examples of recycled polyurethanes in food packaging have been addressed, however the recycling of polyurethane foams is carried out on an industrial scale. Glycolysis is the most common method of de-formulation in polyurethanes to produce the raw materials which are often re-formulated for foam applications. Although polyurethane adhesives do not come into contact with the foodstuff the possible application of these recycled products should still be monitored to ensure consumer safety.

The development of a one-step extraction and concentration method for laminate migrants was considered and pre-liminary work was attempted. The idea is to carry out one extraction on the laminate and one concentration step using solid phase extraction while splitting the residue into its three components. All of the simulant containing the migrated species from the polyurethane adhesive was eluted onto the SPE column where the migrants were retained and then separated using different concentrations of an organic solvent in this case methanol (25%, 50%, 75% and 100%) Analysis of the initial elutions of the different solvents only produced data for the polyol component which was detected by MALDI-MS in the 100% methanol solution. The overall migration tests showed the ability of the SPE column to retain the majority of the laminate migrants and it has the potential to provide a good separation step.

Further work into the analysis of migrants from polyurethane adhesives should be focused on polyester based polyols and additive migration. Although cyclic polyester oligomers were identified in the migrants by MALDI-TOF-MS, direct quantification was impossible with the equipment available and with no functionality on the migrant molecules, derivatisation was ruled out. HPLC anayses could be carried where the polyester contained an aromatic ring incorporated into the molecule or by the use of LC-MS detection. HPLC could also be employed for the separation step with an alternative detection method like evaporative-light-scattering detection (ELSD).

Analysis of the non-volatile migrants for the presence of any additives should also be considered possibly using LC-MS to detect both the additive and possible degradation products of the additives in the polyurethane system.

REFERENCES

[1] Polyurethane, chemistry, technology and properties. 1964
Philips L N, Parker D B V. Iliffe Books Ltd, London

[2] Handbook of Adhesives. 3rd edition. 1990
Skeist I, Van Norstrand Reinhold, New York

[3] Polymer science dictionary. 1990
Alger M S M, Elsevier Applied Science, London and New York

[4] The ICI polyurethane handbook. 2nd edition. 1990
Woods G, John Wiley and sons

[5] Panda R, Panda H, *Chemical weekly*, Adhesives and sealants
January 1993, 3, pp 139-136

[6] Kirk-Othmer encyclopaedia of chemical technology, 4th edition, 1997
Krosch J I, volume 24, John Wiley and sons, New York

[7] Chemistry and technology of isocyanates, chapter 2. 1996
Ulrich H, John Wiley and sons

[8] Fundamental chemistry and catalysis of polyurethanes. chapter 1. 1969
Frisch K C, Bruins P F, Interscience Publications,
John Wiley and sons, New York

[9] Beachell H C, Nogoc Son C P, *Journal of applied polymer science.*
1963, 7, pp 2217

[10] Beachell H C, Nogoc Son C P, *Journal of applied polymer science.*
1964, 8, pp 1089

[11] Kirk-Othmer encyclopaedia of chemical technology, 4th edition, 1996
Krosch J I, volume 19, John Wiley and sons, New York

[12] Bonell A E, Lawson G. List of substances used in the manufacture of adhesives
for food packaging in the UK. May 1998, MAFF project FS2223

[13] Ullman's encyclopaedia of industrial chemistry. 5th edition. volume A21, 1993.
Elvers B, Hawkins S, Schulz G. V.C.H

[14] Barkby C T. Migration from non-ovenable food contact materials at elevated temperatures. Thesis. De Montfort University, Leicester. 1993

[15] Plastic packages for foodstuffs. A topical survey of legal regulations and migration testing. 1996. Figge K. Wissen Schaftliche Verlagsgesellschaft mbH

[16] Bonell A E. Polyurethane adhesives in food pakaging
Handout. January 1998

[17] Classification of packaging adhesives. *Industrial packaging adhesives*
Lazarus D M. pp 20-43. FSL 0106

[18] Ward R J. *Adhesives age*, 1970. pp 26

[19] Adhesion of urethanes from oxypropylene polyol 'advances in urethane science and technology'. 1973. Reegen S L, Frisch K C, volume 2, No 56,
Technorric, Stamford

[20] Solventless adhesives for packaging laminations (17) - Seminar, 1992
Schetschok H G, Morton International GMBH

[21] Migration and sorption phenomena in packaged foods.
Gnanase-Kharan V, Floros J D. *Critical reviews in food science and nutrition.*
volume 37, No 6, pp 519-559, 1997

[22] Practical guide N 1; CS/PM/2024. 2nd April 1993

[23] Plastic materials and srticles intended to come into contact with foodstuffs.
Directive 90/128/EEC. *Official journal of the European communities*, No L75
21st March 1990

[24] Methods of test: Plastic migration. Directive 82/711/EEC. *Official journal of the European communities.* No L297/26, 18th October 1982

[25] Testing migration, 1st amendment to Directive 82/711/EEC. Directive 93/8/EEC.
Official journal of the European communities. 1993

[26] List of simulants to be used for testing migration of constituents of plastic materials and articles intended to come into contact with foodstuffs.
Directive 85/572/EEC. *Official journal of the European communities.*
No L372/14, 19th December 1985

[27] Positive list of additives used in plastics, 3rd amendment to Directive 90/128/EEC. Directive 95/3/EEC. *Official journal of the European communities.* 1995

[28] Positive list of additives used in plastics, 4th amendment to Directive 90/128/EEC. Directive 96/11/EEC. *Official journal of the European communities.* 1996

[29] Rossi L. *Food addtives and contaminants.* 1988, 5, 543

[30] Rossi L. *Food addtives and contaminants.* 1988, 5, 21

[31] Food contaminants: sources and surveillance. 1991
Creaser C, Purchase R. The royal society of chemistry

[32] Van Battum D, Rijk M A H, Verspoor R, Rossi L. *Food chem toxic.* volume 20, pp 955-959, 1982

[33] The suitability of alternative fatty food simulants for overall migration testing under both low and high temperature test conditions. De Kruif N, Rijk R. *Food additives and contaminants.* volume 14, No 6-7, pp 775-789, 1997

[34] De Kruijf N, Rijk M A H, Soetardhi L A, Rossi L. *Food chem toxic,* volume 21, pp 187-197, 1983

[35] De Kruijf, Rijk M A H. *Food additives and contaminants,* volume 5, No 1, pp 467-483, 1988

[36] The evaluation of global migration and the assessment of related parameters by spectrophotometric methodology. Lox F, DeSmet R, Walden A, Machiels V. Packaging technology and science, volume 1, pp 11-16, 1988

[37] An improved olive oil overall migration test for plastics using karl fischer titrations. Castle L, Hedgcock S E, Kwiatkowska C A, Sharman M, Smith I D *Food sdditives and contaminants,* volume 9, No 1, pp 11-17, 1992

[38] An ultraviolet spectrophotometric method as an alternative test for determining overall migration from aromatic polyester packaging materials into fatty food oils. Reeves B J. *Food sdditives and contaminants.* volume 14, No 6-7, pp 591-599, 1997

[39] Contaminant migration from food packaging laminates used for heat and eat meals. Lawson G, Barkby C T. Lawson C. *Fresenius journal of analytical chemistry.* volume 354, pp 483-489, 1996

[40] Swensson A, Holmquist C, Lundgren K. *Brit j indust med*, volume 12, pp 50, 1955

[41] Marcali K. *Analytical chemistry*, volume 29, No 4, pp552, 1957

[42] High performance liquid chromatographic determination of 2,4- and 2,6- toluene diamine in aqueous extracts. Snyder R C, Breder C V, *journal of chromatography*, volume 236, pp 429-440, 1982

[43] An improved HPLC method for the determination of isocyanates using 'nitro-reagent'. Hakes D, Johnson G, Marherka J. *Am ind hyg Assoc J.* volume 47, No 3, pp 181-184, 1984

[44] Determination of polymethylenepolyphenylene isocyanate in air by size exclusion chromatography. Beasley R K, Warner J M. *Anal chem*, volume 56, pp 1604-1608, 1984

[45] Determination of complex mixtures of airbourne isocyanates and amines. Spanne M, Tinnerberg H, Daleno M, Skarping G. *Analyst*, volume 121, pp 1095-1099, 1996

[46] Liquid chromatographic determination of residual isocyanate monomers in plastics intended for food contact use. Damant A P, Jickells S M, Castle L. *Journal of AOAC international*, volume 78, No 3, pp 711-719, 1995

[47] Brand new technology in lamination offers ultra fast curing properties as well as faster aromatic amine decay. Curex Aps. Denmark. 1997

[48] Campbell G A, Meluch W C. *Journal of applied polymer science*, 21, 581, 1977

[49] Decomposition of polyurethane foams by alkanolamines. Kanaya K, Takahashi S. *Journal of applied polymer science*. volume 51, pp 675-682, 1994

[50] Bauer G. Polyurethane world congress 1991. September 24-26, pp 872-876

[51] Simioni F, Modesti M, Rienzi S A. *Cell polm*, 6, pp 2741, 1987

[52] Migration of primary aromatic amines from laminates into test food. Zeneca specialities, Hamburg. Analytical method No 032, 1996

[53] HPLC and detection of polyethers and their mono(carboxy)alkyl and arylalkyl sustituted derivatives. Rissler K. *J of chromatography A*, 742, pp 1-54, 1995

[54] Martin N. *Journal of liquid chromatography*, 18, pp 1173, 1995

[55] Trathrigg B, Thamer D, Yan X, Kinugasa S. *Journal of liquid chromatography*, 16, pp 2439, 1993

[56] Murphy R, Selden A C, Fisher M, Fagen E A, Chadwick V S. *Journal of chromatography*, 211, pp 160, 1981

[57] Kinahan I M, Smyth M R. *Journal of chromatography*, 565, pp 297, 1991

[58] Desberie, Desmaizieres B. *Journal of chromatogrphia A*, 661, 207, 1994

[59] Rissler K, Fuchslueger, Grether H J. *Journal of liquid chromatography*, 17, pp 3109, 1994

[60] Analysis of ethoxylated alcohol surfactants in water by HPLC. Nitschke L, Huber L. *Fresenius j of analytical chemistry*, 345, pp 585-588, 1993

[61] Lemr K, Zanette M, Marcomini A. *J of chromatography A*, 686, pp 219, 1994

[62] Application of liquid chromatography-thermospray mass spectrometry to the analysis of polyester oligomers. Guarni A, Guglielmetti G, Po R. *Journal of chromatography*, 647, pp 311-318, 1993

[63] Barnes K, Damant A, Startin J, Castle L. *Journal of chromatography A*, 712, pp 191, 1995

[64] Migration from boil-in-bag laminates. Lawson G. 1994 Food science reviews, volume 2. Chemical migration from food packaging. Ellis Harwood series in food science technology

[65] Milon H. *Journal of chromatography*, 554, pp 305, 1991

[66] Kniger R, Much H, Schultz G. *J of liquid chromatography*, 17, pp 3069, 1994

[67] Kniger R, Much H, Schultz G, Wachsen O. *Macromol symp*, 110, pp 155, 1996

[68] Online extraction of polymers, oligomers, additives and monomers by multiple solvents on packed HPLC columns. Stall W J, Cools P , Van Herk A , German A. *Chromatogrphia*, volume 37, No 3/4

[69] Supercritical fluid extraction - supercritical fluid chromatography- mass spectrometry for the analysis of addtives in polyurethanes. Makay G A, Smith R M. *Journal of chromatogrphic science*, volume 32, pp 455-460, 1994

[70] A reversed-phase high pressure liquid chromatographic method for analysis od additives in polyolefins. Haney M A, Dark W A, *Journal of chromatographic science*, volume 18, pp 655-659, 1980

[71] Analysis of addtives in plastics by high performance size exclusion chromatography. Shepherd M J, Gilbert J. *Journal of chromatography*, 218, pp 703-713, 1981

[72] TOF static secondary ion mass spectrometry of additives on polymer surfaces. Mawn M P, Linton R W, Bryan S R, Hagenhoff B, Jurgens V, Benninghoven A. *Journal of vacuum science technology*, volume A9, No 3, pp 1307-1311, 1991

[73] MALDI-TOF mass spectrometry in the anlysis of synthetic polymers. Rader H J, Schrepp W. *Acta polymer*, 49, pp 272-293, 1998

[74] Industry urges more flexibility. Food packaging laws. *European chemical news* pp 24, 16-29 December 1996

[75] Recycled polymers in food packaging: Migration considerations. Begley T H, Hollifield H C. *Food technology*. ppg 109-112, November 1993

[76] Feedstock recycling: new plastic for old. *Chemistry in britain* pp 515-517, July 1995

[77] Quality and safety aspects of reusable plastic food packaging materials. Jetten J, De Kruijf N, Castle L. *Food additives and contaminants*, volume 16, No 1, pp 25-36, 1999

PAGE NUMBERING AS ORIGINAL

The Analyst
FULL PAPER

MALDI-MS and colorimetric analysis of diisocyanate and polyol migrants from model polyurethane adhesives used in food packaging†

Graham Lawson,* Sally Bartram, Sylvia Fitchner and Elaine D. Woodland

Department of Chemistry, De Montfort University, The Gateway, Leicester, UK LE1 9BH

Received 13th August 1999, Accepted 4th October 1999

The identification of the migrants, into food simulants, from a series of polyurethane adhesives used in the manufacture of plastic film laminates for use in common food packaging is described. Commercial materials, based on four different model adhesive systems, were prepared by an industrial collaborator. The MALDI-MS fingerprint patterns of the three polyether and one polyester polyol components of these adhesives were obtained for reference purposes. The decrease in the level of diisocyanate as a migrant *versus* time after lamination was confirmed by colorimetric measurements. The migration of the standard polyol samples through polyethylene pouches into water at 70 °C has been demonstrated and also the attenuation effect for different polyols. Cured laminates in the form of pouches were used to carry out the migration experiments into distilled water, inside the pouch, at 70 °C over a period of 2 h. Comparison of the migration results from the food packaging laminates with those from the polyethylene film confirmed the migration of unreacted polyol components for the polyether-based systems. Cyclic oligomers from the polyol starting materials were identified as the migrants from the polyester-based adhesive.

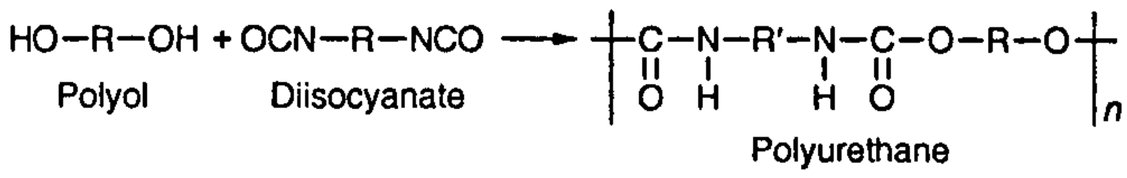
Introduction

There is considerable current concern about the safety of food and its packaging. Plastic packaging is closely regulated for use in food contact applications,[1–3] but there is currently no UK or EU legislation relating specifically to adhesives used in this area. The finished item would however be subject to the general provisions of the Materials and Articles in Contact with Food Regulations.[1] There has been little work reported on the analysis of migrants from food packaging adhesives into food simulants. Gruner and Piringer[4] have carried out quantitative studies on migrants from adhesives used in the paper and board packaging sector, but no chemical compounds were identified. The gravimetric determination of the overall migrants from polyurethane-based laminates into several food simulants has been reported by Lawson *et al.*[5]

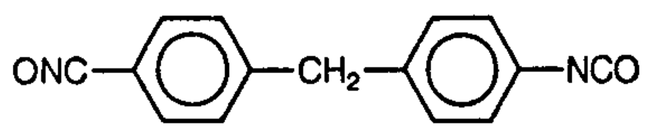
This investigation has concentrated on the analysis of migrants from a range of polyurethane (PU) adhesives used to bond two films together to form a laminate. Laminates are required when an individual film cannot meet the demands of the foodstuff or storage and preparation requirements. For example, polyethylene (PE) is often used as it can be heat-sealed, but it offers limited odour, flavour and gas barrier properties, whereas polyethylene terephthalate (PET) offers good gas barrier properties. Laminates of two such materials are used as bags for ground coffee, packs for smoked salmon, pouches for alcoholic cocktails and to package frozen boil-in-the-bag meals.

Matrix-assisted laser desorption/ionisation mass spectrometry (MALDI-MS) is a relatively new soft ionisation technique capable of looking at sample mixtures over a mass range of 150–500 000 Da without prior separation. It has been applied over the past 5 years to the analysis of synthetic polymers because of its ability to measure oligomeric distributions. MALDI generally produces singly charged ions and facilitates the measurement of extremely high molecular weights with virtually no fragmentation and enables determination of repeat units and end group composition.[6,7] This technique was used to identify the principal components of the species migrating from the PU adhesives.

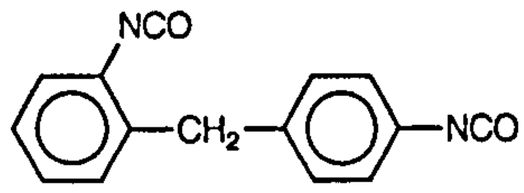
PU adhesives are reactive systems produced by the addition reaction of a polyol and a polyisocyanate:



PU adhesives used in food packaging in the UK are usually derived from diphenylmethane diisocyanate (MDI)

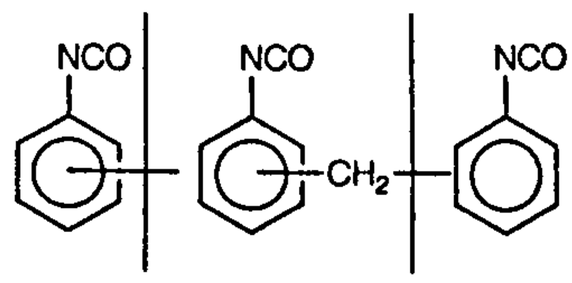


4,4′-MDI



2,4′-MDI

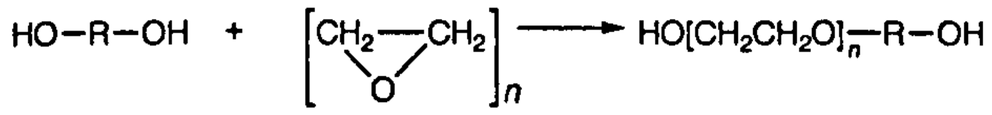
Common solvent-free adhesive formulations contain a mixture of the different monomers in solution in polymeric MDI (PMDI) which has a general structure:



Approximately 2400 tonnes of PU adhesive are used annually in Europe for solvent-free laminations, whilst another 2200 tonnes[8] of the adhesive are used for similar purposes, but are prepared in solution in either a ketone or ethyl acetate.

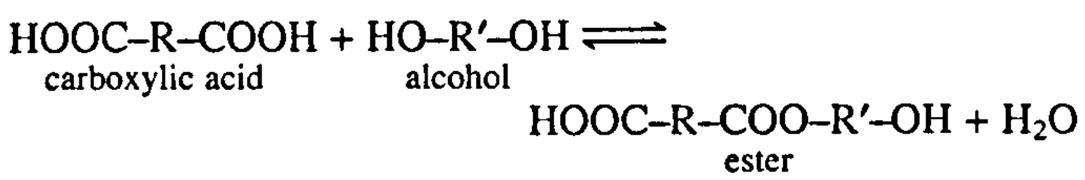
† Presented at SAC 99, Dublin, Ireland, July 25–30, 1999.

The polyol component of the PU adhesive can be either a polyfunctional polyether or polyester, a mixture of both or castor oil. In all cases, for use in flexible adhesives the molecular mass of the polyol component is in the range 400–2000. Polyether polyols are produced by the addition of either ethylene oxide or propylene oxide to a polyhydroxy 'starter' molecule in the presence of a catalyst:



Typical starter molecules include glycerol, ethylene glycol, propylene glycol and trimethylolpropane.

Polyester polyols are produced by the condensation reaction of polyfunctional carboxylic acids or anhydrides with polyfunctional alcohols



In commercial applications it is common to find polyesters prepared from a mixture of two or more acids reacted with two or more glycols, which gives scope for a range of very complex products. Typical materials used in a single 'simple' commercial polyol formulation include diethylene glycol, neopentyl glycol, adipic acid and isophthalic acid. Both the polyether and polyester polyol components will therefore contain a range of oligomeric material and also any stabilisers, pH adjusters and other additives, any of which may be potential migrants once the laminating process has been completed.

Clearly, a PU adhesive is a complex material which starts as a mixture of the diisocyanate and free polyol as the bonding layer between two plastic films. This mixture cures with time and hence the species available for migration will change from the original starting materials to final reaction products and residues. The Flexible Packaging Association (FPA), the trade association representing the manufacturers of this type of packaging, have a code of practice which recommends that all such PU bonded laminates are stored for 7 d prior to dispatch. This delay after lamination ensures that the residual diisocyanate level has decayed to less than 1 ppm in order to meet the current plastics regulations.[2]

Experimental

Migration experiments were carried out using commercially prepared PET–PU–PE films heat-sealed into pouches. The food simulants were placed in the pouch and migration into the pouch contents was investigated. In the course of this study using model commercial PU adhesives, the level of migratable diisocyanate as a function of time after lamination was studied to determine the time after which the material would be considered cured (< 1 ppm diisocyanate). A MALDI-TOF mass spectrometer and colorimetric methods were used to study the species migrating into different food simulants from the cured laminate. Experiments were also carried out to confirm the poor barrier properties of the PE film to liquid polyols.

Packaging samples

All the laminates used in this investigation were prepared commercially using 12 μm PET bonded to 45 μm low-density PE with a range of different PU adhesives. The commercial preparation of the samples ensured the quality of the laminate, particularly the correct adhesive coat weight within the range 1–2.5 g m^{-2} as appropriate to each adhesive formulation. The adhesives were simplified versions of commercial products based on monomeric and polymeric MDI with known polyol formulations. The samples were supplied by industrial collaborators.

Migration experiments

Pouch samples (20 × 20 cm) were prepared by heat-sealing the laminate with the PE as the inner layer next to the different food simulants. Similar pouches, made from the PE film used as the inner layer of the laminate, were prepared for the liquid polyol migration studies. The food simulant used was Millipore (18 MΩ) water. The pouch laminates containing 100 cm^3 of food simulants were placed in the oven for 2 h at 70 °C. After this time the simulant was removed and concentrated to 10 cm^3 using a rotary evaporator at 60 °C. For the polyol migration studies the simulant was the water surrounding the pouch.

Reagents

The following reagents were used: Millipore water (resistivity 18 MΩ cm, Milli-RO15 water system); analytical-reagent grade acetic acid and hydrochloric acid, *N*-(1-naphthyl) ethylenediamine dihydrochloride (NEDD), 4,4′-methylenedianiline (MDA) and aniline hydrochloride (Fisher Scientific, Loughborough, Leicestershire, UK); sodium nitrite (Sigma-Aldrich, Gillingham, Dorset, UK); ammonium sulfamate (Merck/BDH, Lutterworth, Leicestershire, UK); and polypropylene oxide (ICI Surface Coatings, Birmingham, UK).

Colorimetric determination of primary aromatic amines

A Unicam UV-2-100 UV/VIS spectrometer, equipped with a 40 mm pathlength (silica) cell and operated at a wavelength of 550 nm, was used.

The following solutions were used:

Acid solution. 0.3 M acetic acid–0.5 M hydrochloric acid.

Sodium nitrite. 0.25 g in 50 cm^3 of water.

Ammonium sulfamate. 2.5 g in 100 cm^3 of water.

Coupling reagent. NEDD, 0.5 g in 50 cm^3 of water.

MDA. 50 μg in 100 cm^3 of water.

Aniline hydrochloride. 50 μg in 100 cm^3 of water.

Under the experimental conditions any migrating diisocyanate would be hydrolysed to the corresponding diamine, which can then be detected colorimetrically using a diazotisation reaction based on the work of Marcali.[9,10] Freshly prepared laminate, less than 4 h after lamination, was collected from the converters, returned to the laboratory and subjected to the migration experiments detailed above on a twice daily basis for 14 d. After extraction, the aqueous food simulant was removed from the pouch and rotary evaporated under vacuum at 60 °C to 10 cm^3; the derivatisation step was then carried out as follows: 5 cm^3 of acid solution and 2 cm^3 of acetone were added to the concentrated simulant; 1 cm^3 of sodium nitrite solution was added and left for 10 min. After this, 2 cm^3 of ammonium sulfamate were introduced and left to react for a further 10 min; then, 2 cm^3 of coupling reagent were added and the colour was

allowed to develop for 2 h before measurement at 550 nm. These measurements were replicated and the concentration of MDA was determined from a calibration graph prepared from authentic MDA. A simple calculation allowed the mass of the migrating MDI to be calculated from the measured mass of MDA.

MALDI-MS analysis

A Finnigan Lasermat-2000 linear time-of-flight mass spectrometer, equipped with a N_2 laser pulsed at 337 nm, was used.

MALDI-MS only requires 1 μl of sample (concentration 10^{-5}–10^{-7} M) to be dried with a selected matrix and placed in the ion source. A UV laser then volatilises/ionises the sample and matrix; ionisation occurs during volatilisation by energy transfer between matrix and analyte. Gentisic acid (2,5-dihydroxybenzoic acid) was employed as the matrix in this investigation. A 1 μl aliquot of sample was mixed with 1 μl of matrix (concentration 1 g l^{-1} in water) and dried for analysis.

Results

Residual isocyanate moiety expressed as the amine

The results obtained (Fig. 1) show that the migratable isocyanate level reaches 1 ppm approximately 50 h after lamination. The FPA recommended time delay is shown on Fig. 1 to indicate the anticipated migratable NCO level from a typical commercial laminate. These results show that the level of NCO moiety migrating from the laminate is well below that expected from the EU specified residual level of 1 ppm free NCO moiety.

MALDI-MS analysis of polyol standards

The mass spectra of the polyether samples (mean molecular weights 500, 1000 and 2000) showed a clear distribution of oligomers centred on the expected molecular weight; see for example the spectrum from polyol 2000 (Fig. 2).

The spacing between peaks of 58 units corresponds to a propylene oxide [$CH_2CH_2(CH_3)O$] unit and the shoulders on the low mass peaks result from the sodium adduct ions $(M + 23)^+$ of the corresponding oligomer. The spectrum of a simple polyester polyol based on adipic acid (AA) and diethylene glycol (DEG) showed a much wider mass range, 500–5000, due to the (AA–DEG) repeat unit with a mass of 216. Furthermore, the molecular weight distribution was asymmetric with a long tail at high mass. These traces were used as reference data for the subsequent migration experiments.

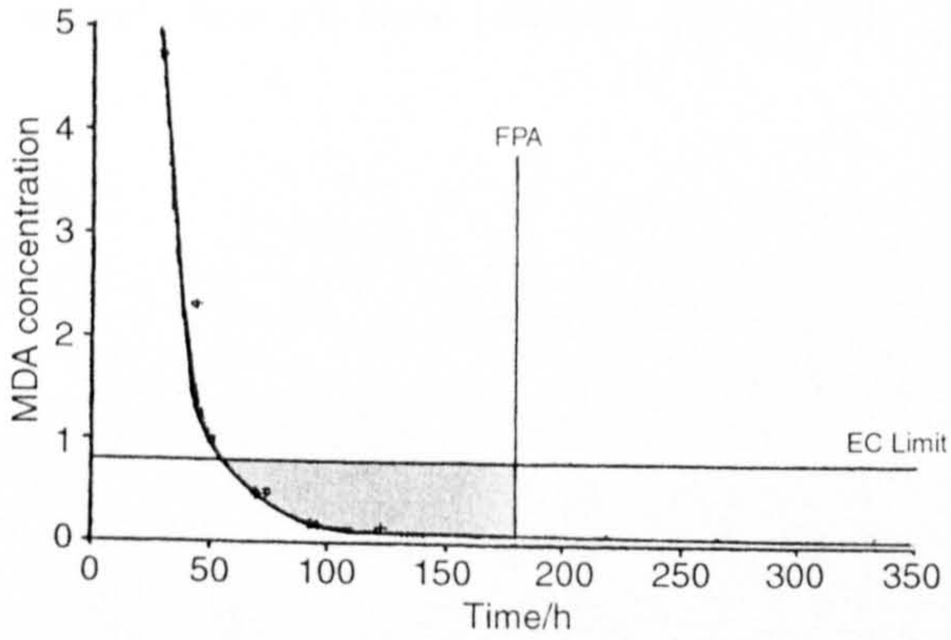


Fig. 1 MDA concentration in a food simulant *versus* time after lamination for a commercial laminated pouch.

Migration through PE films

MALDI analysis (Fig. 3) of the components of polyols which can migrate through a 45 μm PE film demonstrates that bifunctional polypropylene oxide systems with molecular weights up to 1600 can readily migrate with little change in the relative abundance of the oligomers. Trifunctional polyether systems (Fig. 4) show a much lower potential for migration (limit about 600 mass units) and there is a clear change in the relative abundance of the oligomers after passage through the film. There is a similar attenuation of the migrating oligomers from the polyester polyol. Fig. 5 compares the full range of oligomers (upper trace) with those capable of passage through the PE film (lower trace). These results clearly demonstrate that the PE film used in commercial laminates presents little barrier to polyol migration where the liquid material is present.

Migrants from commercial pouch samples

For commercial samples composed of polyether polyols, the MALDI mass spectra are similar to, or identical with, those shown in Fig. 2, whereas for the polyester polyols the MALDI data did not correspond to those shown for the liquid polyol. The migrants from the polyester-based laminate showed no detectable evidence of the anticipated oligomers. The only migrants observed (Fig. 6) have been identified, by synthesis

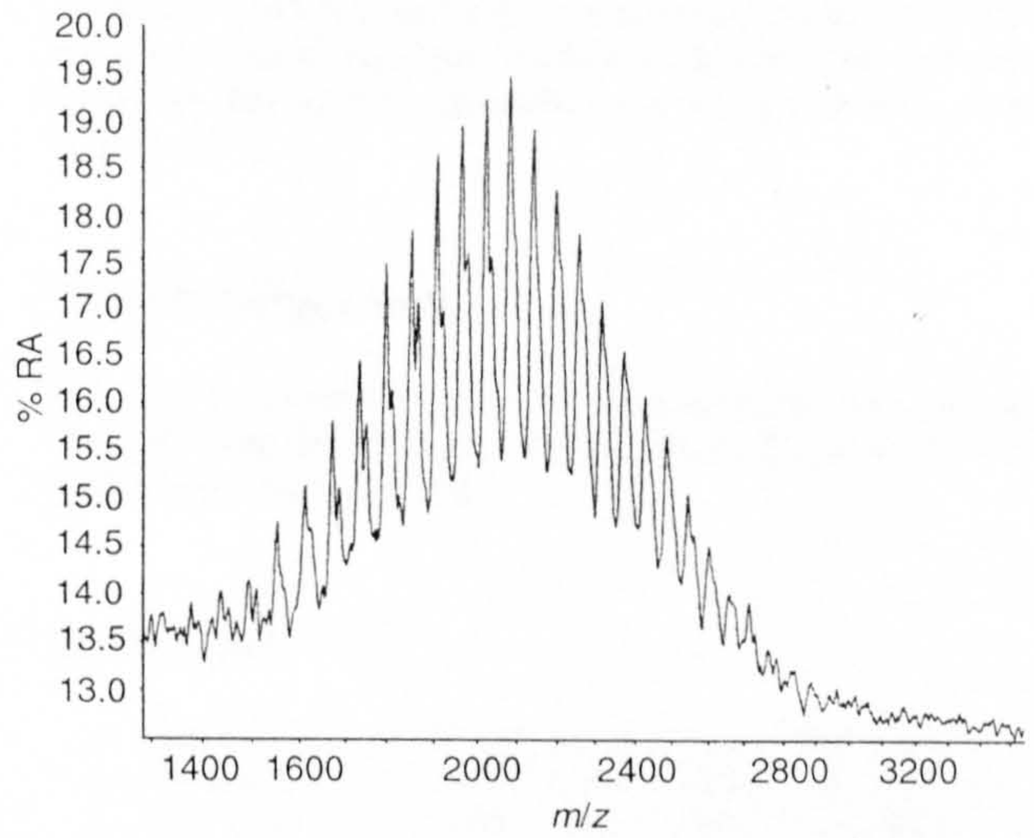


Fig. 2 MALDI mass spectrum of a liquid polypropylene oxide polyether polyol (M_w 2000). (%RA = per cent relative abundance)

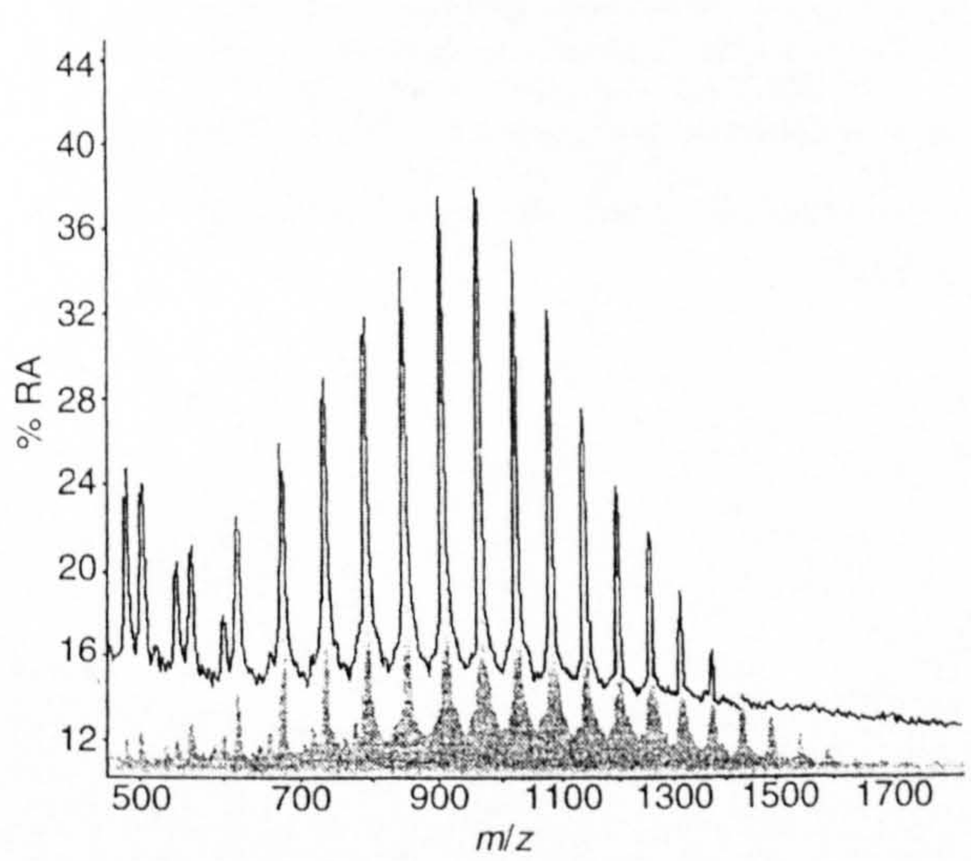


Fig. 3 MALDI mass spectrum of liquid bifunctional polypropylene oxide (M_w 1025) before (top trace) and after (bottom trace) migration through 45 μm low-density PE film into water.

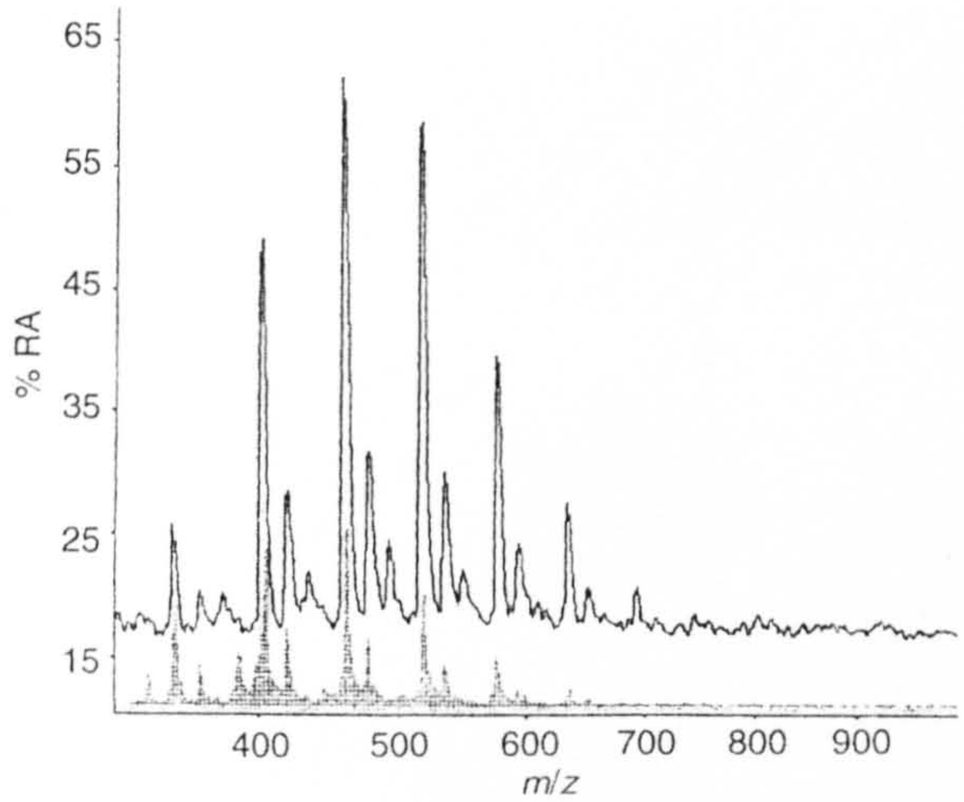


Fig. 4 MALDI mass spectrum of liquid trifunctional polypropylene oxide (M_w 440) before (top trace) and after (bottom trace) migration through 45 μm low-density PE film into water.

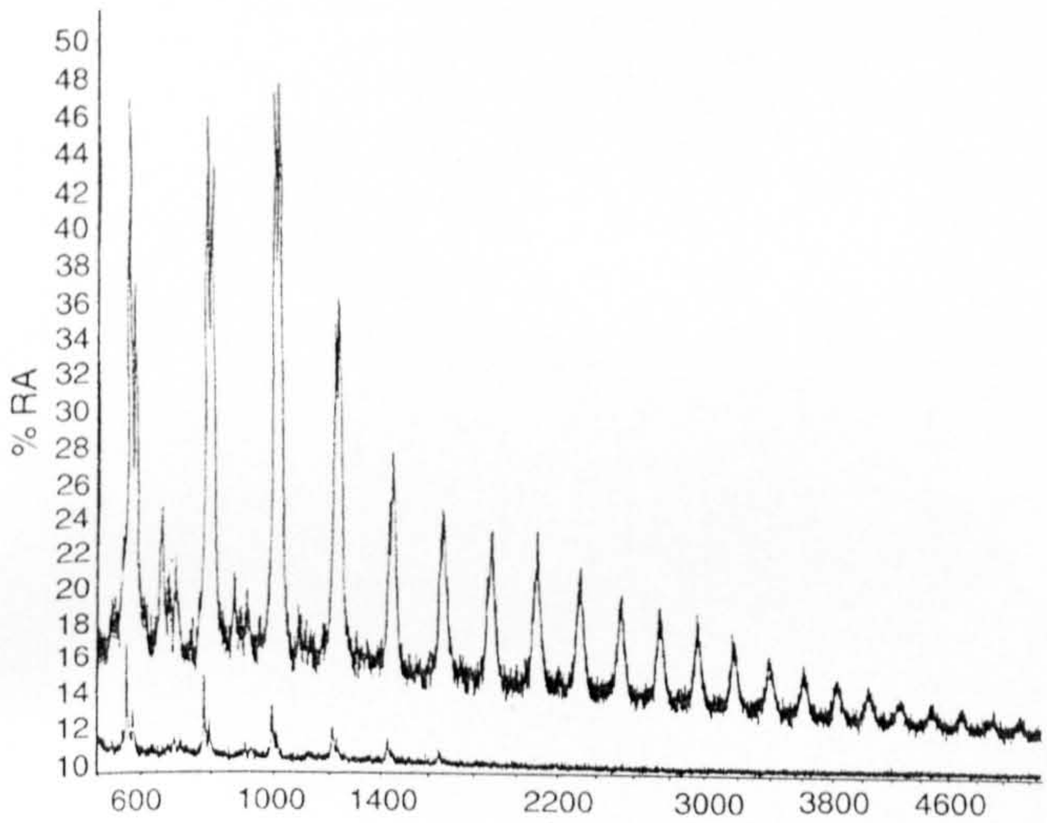


Fig. 5 MALDI mass spectrum of a simple liquid polyester polyol, before (top trace) and after (bottom trace) migration through 45 μm low-density PE film into water.

and LC-MS analysis, as cyclic oligomers which have no hydroxyl functionality and therefore cannot be 'locked into' the polymer backbone by reaction.

Conclusions

MALDI-MS provided rapid meaningful analyses of both the reference polyol sample and the products of migration.

The only MALDI-MS detectable species present in the migrants from PU-based adhesives are oligomers from the polyol component of the adhesive. This is a surprising result since the PU formulations are used with an excess of diisocyanate which is consumed by atmospheric moisture during the curing process. Hence, some polyol must dissolve in the PE film prior to reaction and this is isolated from the diisocyanate and is therefore free to migrate. This argument does not however explain why no linear polyester oligomers are observed.

MALDI-MS measurements cannot readily be quantified and therefore a derivatisation methodology must be developed to facilitate the HPLC quantification of the levels of polyol migration.

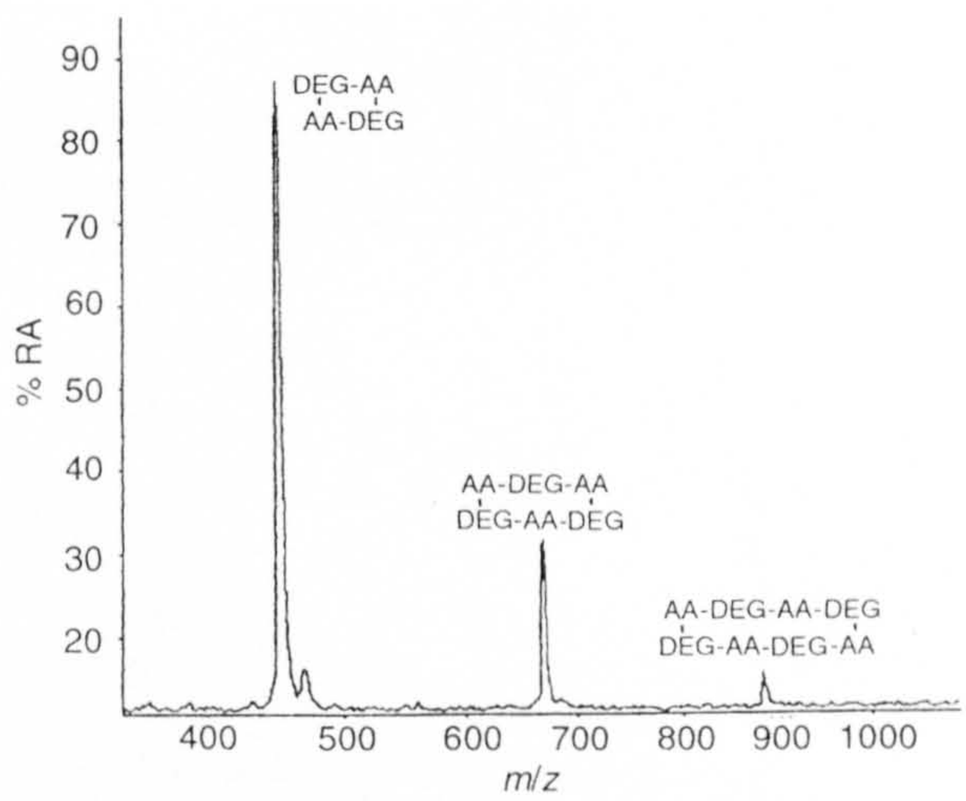


Fig. 6 MALDI mass spectrum of the migrants from a laminate bonded with a PU containing a simple polyester-based polyol.

Acknowledgements

S.F. was financed under the Socrates scheme. Financial support for S.B. from the Ministry of Agriculture, Fisheries and Food is gratefully acknowledged.

References

1 EEC Directive 89/109, *Off. J. Eur. Comm.*, 1989, **L40**, 38.
2 EEC Directive 90/128, *Off. J. Eur. Comm.*, 1990, **L349**, 26.
3 EEC Directive 92/39, *Off. J. Eur. Comm.*, 1992, **L168**, 21.
4 A. Gruner and O. Piringer, *Packag. Technol. Sci.*, 1999, **12**, 19.
5 G. Lawson, C. T. Barkby and C. Lawson, *Fresenius' J. Anal. Chem.*, 1996, **354**, 483.
6 H. J. Rader and W. Schrepp, *Acta. Polym.*, 1998, **49**, 272.
7 P. Zollner, G. Stubinger, F. Schmid, E. Pittenauer and G. Allmaier, *Int. J. Mass Spectrom. Ion Processes*, 1997, **169**, 99.
8 T. Cadby, ICI Surface Coatings, personal communication.
9 K. Marcali, *Anal. Chem.*, 1957, **29**, 552.
10 C. T. Barkby, PhD Thesis, De Montfort University, 1995.

Paper a906595d